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Vapor-Liquid Equilibrium of Binary Mixtures in the Extended Critical Region

I. Thermodynamic Model

James C. Rainwater

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I. Thermodynamic Model

James C. Rainwater

Thermophysics Division
Center for Chemical Engineering
National Engineering Laboratory
National Institute of Standards and Technology
Boulder, Colorado 80303-3328



U.S. DEPARTMENT OF COMMERCE, Robert A. Mosbacher, Secretary
NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY, Raymond G. Kammer, Acting Director

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Vapor–Liquid Equilibrium of Binary Mixtures in the Extended Critical Region

I. Thermodynamic Model

by

James C. Rainwater

The thermodynamic model of Leung and Griffiths for binary mixture vapor–liquid equilibrium near the critical locus, as modified by Moldover, Rainwater and co-workers, is extended to accommodate fluid pairs of greater dissimilarity. The maximum absolute value of a dimensionless ratio of composition difference to density difference (α_{2m}) is shown to be a very useful measure of dissimilarity of components. New parameters are introduced into the model with guidelines that the number of permissible parameters depends on, and increases with, α_{2m} . The quantity K in the Leung–Griffiths fugacity ratio ζ is generalized from a constant to a temperature–dependent function. Among other consequences, the previously approximate relation that the mole fraction $x = 1 - \zeta$ on the critical locus can for most mixtures be made exact. For $\alpha_{2m} < 0.25$, an empirical principle is asserted which predicts a relationship between the critical slopes of constant–composition curves on temperature–density plots or isotherms on density–composition plots and derivatives of critical locus parameters. The coexistence surface is shown to be insensitive to $dx/d\zeta$ on the critical locus at the dilute limits. The range of the model is extended to $\alpha_{2m} \approx 0.3$, e.g. propane + n-octane or carbon dioxide + n-butane. The modified model is contrasted with conventional equation–of–state methods and with the original Leung–Griffiths formalism.

Key words: binary mixtures; coexisting densities; corresponding states; critical region; dew–bubble curves; field variables; Leung–Griffiths model; scaling–law exponents; vapor–liquid equilibrium

1. Introduction

The accurate correlation of vapor-liquid equilibrium (VLE) in the critical region has long been recognized as an important and inadequately resolved problem. Rowlinson and Swinton note at several places throughout their book Liquids and Liquid Mixtures [1] that conventional thermodynamic approaches are unsuccessful near a critical locus, and that special mathematical forms for the thermodynamic variables must be utilized in that region. Their final observation, just prior to their "Conclusions" section on the state of liquid theory, is that the model of Leung and Griffiths [2] (as modified by Moldover and Gallagher [3,4]) overcomes in principle the problems of conventional methods and, in particular, yields an accurate fit to the sulfur hexafluoride + propane VLE data of Clegg and Rowlinson [5]. Their last statement is that "this technique could, with advantage, be applied to other systems."

Our objective in this report and Part II of this series is to present and to summarize our progress to date in the fulfillment of the above suggestion by Rowlinson and Swinton. During the decade since the publication of the articles by Moldover and Gallagher [3,4], progress began slowly. In retrospect, this was because their model, while based on an ingenious hypothesis that serves as an excellent starting point for a more generally applicable technique, was in its original form too simple to account for all but a small fraction of binary mixtures.

Within this project, we have endeavored to collect critical region VLE data from all available sources, and have ordered the mixtures according to ease or difficulty of fitting, a concept which is made quantitative later in this report. As we have progressed from the easier to the more difficult mixtures, parameters have been added, but only as necessary. Our system includes a set of guidelines for how many parameters may be used on a given mixture. Accordingly, the model fits VLE data adequately without overfitting, and in many cases can distinguish bad from good data.

Conventional methods are based on an analytic equation of state, i.e. pressure (P) as an analytic function of temperature (T), molar density (ρ), and composition (x). As described in Appendix A, such methods can at best mimic, rather than correctly represent, thermodynamic behavior in the critical region. The Leung-Griffiths approach employs different variables and thus is "unorthodox" in the context of traditional phase equilibrium methodology, and to workers in the field may initially appear confusing or of questionable legitimacy.

Details of the equations were presented in the original Leung–Griffiths paper [2], and completely but briefly for its modified form in Appendix A of Moldover and Gallagher [4]. Subsequent articles [6–8] have presented the model only as recipe, with enough equations so that calculations may be reproduced, but largely without derivation or thermodynamic justification. Meanwhile, the model has undergone significant additional development since the work of Moldover and Gallagher.

There is, therefore, a need for a current and detailed explanation of the theory and techniques, which this report is intended to satisfy. The mostly self-contained exposition should be useful for a novice as well as for an individual, of either scientific or engineering background, experienced in phase equilibrium calculations. Although this first report of a series of two contains many new results and insights not published previously, the primary justification for the work is its wide-ranging success in correlating VLE data as described in Part II of this series.

Furthermore, the Leung–Griffiths formalism is in part rigorous thermodynamics and in part approximation and assumption. Some of our newly introduced parameters can be given heuristic justification, whereas others are purely empirical. The exposition is organized to make clear the logical structure of the method, to identify what is exact and what is approximate, and to present arguments justifying the approximations. In Sec. 2 we define the transformed variables of the Leung–Griffiths model and translate the fundamental laws of thermodynamics into relationships among these variables. The description to this point is general and devoid of assumptions and approximations. With the proper motivation, in Sec. 3 the equation specifying the independent variable (thermodynamic potential), as a function of the dependent variables, is constructed. This step corresponds in the conventional approach to the specification of an equation of state. Specific emphasis is placed on the conformity with simple scaling-law behavior and the thermodynamic consistency of the model. In Secs. 4 and 5, certain heretofore unspecified functions of the independent variables are defined explicitly. The representation of the critical locus in Sec. 6 completes the description of the model. New results and features are summarized in Sec. 7.

In Part II of this series we will present in detail our correlations to four binary alkane mixtures: propane + n-butane, propane + n-pentane, methane + ethane, and (with more limited success) propane + n-octane. We will also summarize and present in tabular form the parameters of successful fits to more than thirty additional binary mixtures.

2. Transformation of Thermodynamic Variables

The system under consideration is a normal, nonazeotropic binary fluid mixture with a continuous VLE critical line joining the two pure fluid critical points. Figures 1 to 4 show schematically the typical phase behavior of such a mixture as projected onto various planes in the P - T - ρ - x thermodynamic volume. Isopleths, or loci of constant composition, are shown in Figs. 1 and 2, and isotherms are shown in Figs. 3 and 4. These figures qualitatively represent most of the VLE data currently available, as isobaric data near critical are very scarce. Note that in P - T space (Fig. 1) the critical locus is the envelope of the constant-composition dew-bubble curves, whereas in P - x space (Fig. 3) the critical locus is the locus of maximum pressure points on the isothermal dew-bubble curves. In the latter case, but not the former, the dew-bubble curves extend slightly outside the critical locus.

Such a mixture is "Class 1" and, in the absence of liquid-liquid equilibrium, "Type 1" according to the classification scheme of van Konynenberg and Scott [9]. The model is also applicable, with some caveats, to azeotropic mixtures and, in some cases, to Class 1 mixtures with liquid-liquid equilibrium (LLE), i.e. Types 2 and 6 mixtures [10], as described later.

Central to the Leung-Griffiths model is the distinction, first made by Griffiths and Wheeler [12], between "field" and "density" variables, and the expectation that the thermodynamics of mixtures is most efficiently represented entirely in terms of field variables. By definition, field variables such as P , T , and the chemical potentials μ_1 and μ_2 , have the same value for coexisting vapor and liquid, whereas density variables, e.g. ρ , have different values. A crucial observation is that the composition x is a density variable, since the vapor is rich and the liquid poor in the more volatile component. Thus equations of state, $P(T, \rho, x)$, are a mixed representation of a field variable as a function of one field and two density variables.

In actual VLE experiments, P , T , x , and in many but not all cases ρ are directly measured; the molar enthalpy, another density variable, is less frequently determined. Except for isolated instances [13], μ_1 and μ_2 are not directly measured and, in the absence of a reliable equation of state in the critical region, must be considered unknown. This creates a dilemma in that a field variable description of thermodynamics necessarily must be expressed in terms of unknown chemical potentials. The dilemma is ultimately resolved

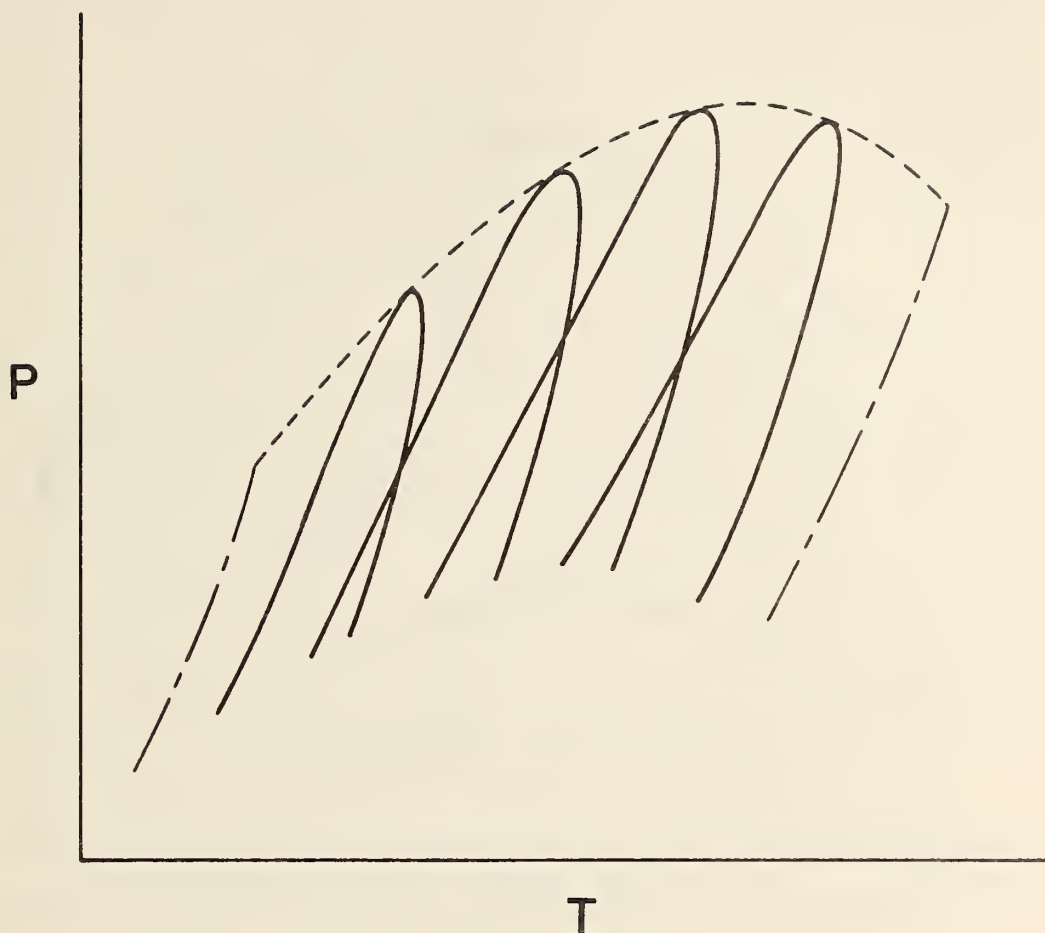


Figure 1. Phase diagram in the P - T plane (schematic). The broken curves are the pure-fluid vapor pressure curves, the dashed curve is the critical locus, the solid curves are dew-bubble isopleths at, for example, $x = 0.2, 0.4, 0.6$ and 0.8 from right to left. In this projection the critical locus is the envelope of the dew-bubble curves.

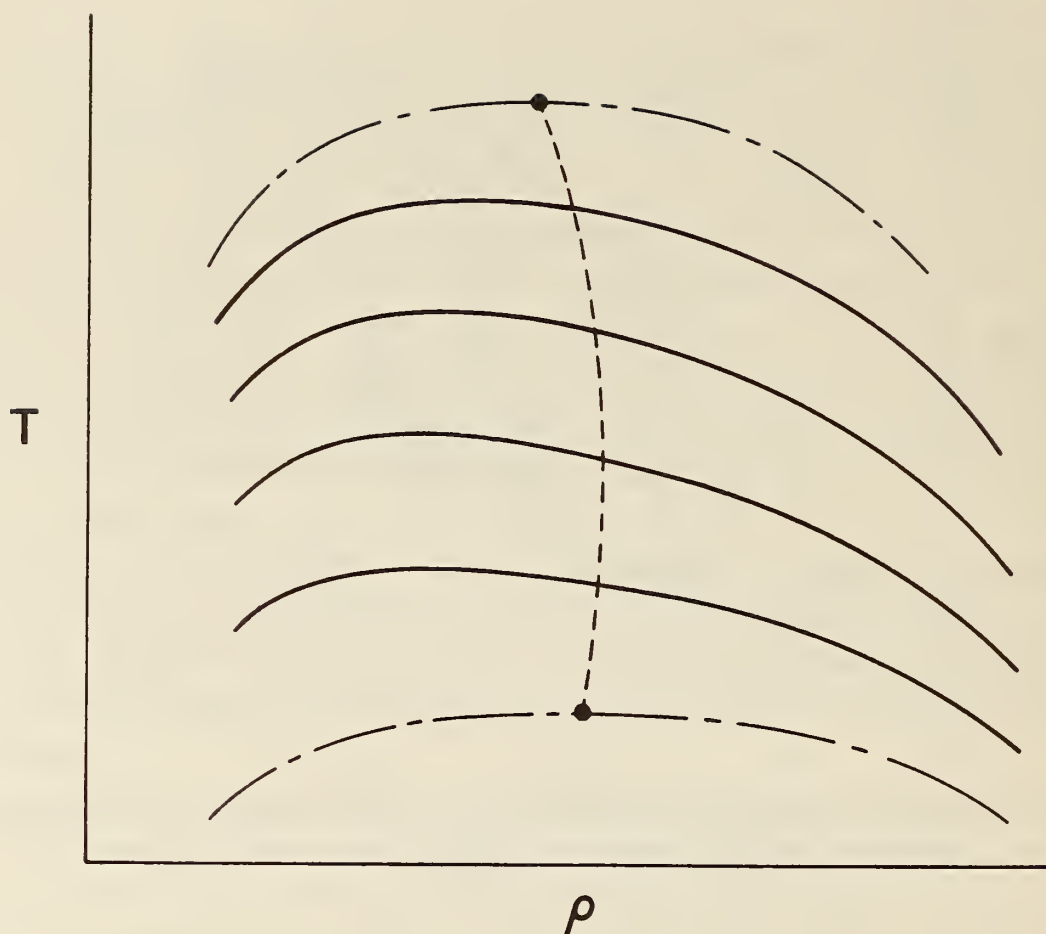


Figure 2. Phase diagram in the T - ρ plane (schematic). The broken curves are the pure-fluid coexisting density curves, the dots are the pure-fluid critical points, the dashed curve is the critical locus, and the solid curves are dew-bubble isopleths at, for example, $x = 0.2, 0.4, 0.6$ and 0.8 from top to bottom.

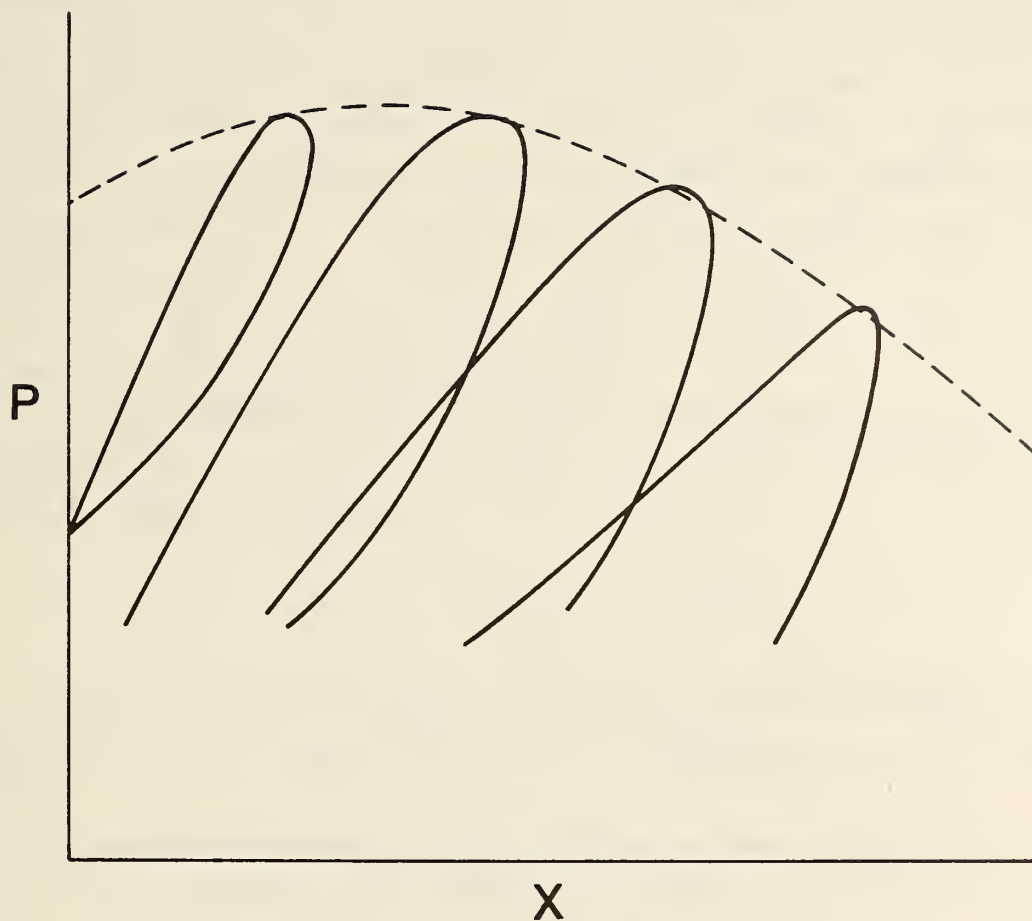


Figure 3. Phase diagram in the P - x plane (schematic). The dashed curve is the critical locus and the solid curves are dew-bubble isotherms at, for example, four evenly spaced temperatures between T_{c1} and T_{c2} with temperature increasing from right to left. In this projection, the critical locus is the locus of points of maximum pressure on the dew-bubble curves. In contrast to Fig. 1, the dew-bubble curves extend slightly outside the critical locus.

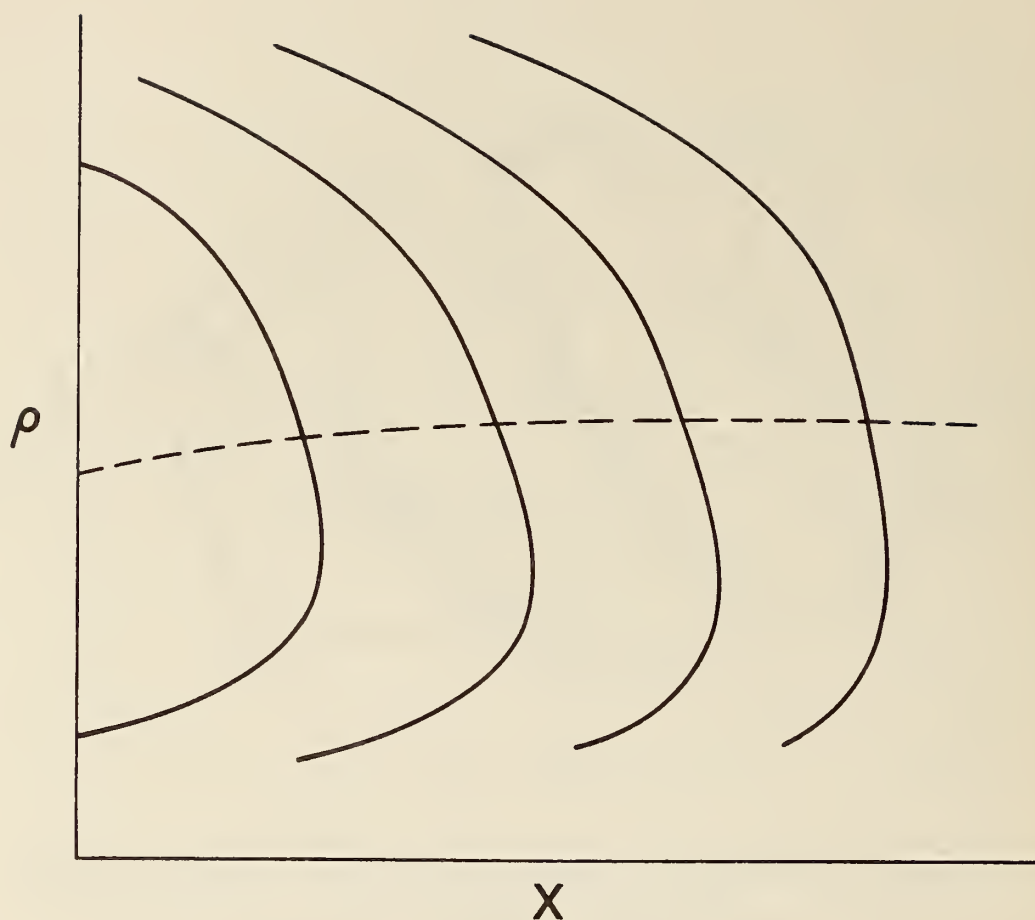


Figure 4. Phase diagram in the ρ - x plane (schematic). The dashed curve is the critical locus and the solid curves are dew-bubble isotherms at, for example, four evenly spaced temperatures between T_{c1} and T_{c2} with temperature increasing from right to left.

by *assuming* a specific parametric dependence of a particular function of chemical potentials on P and T . The statement of this assumption, and its (essentially empirical) justification will be made at the appropriate point in the development.

We acknowledge at the outset that there are many successive transformations of variables which may seem confusing and tedious upon first reading. To the extent possible, we will provide motivation for the introduction of new variables, although their significance can only be fully appreciated *a posteriori*. The objective is to work toward a set of thermodynamic variables in terms of which a mixture most closely resembles a pure fluid, and is thus most efficiently described and correlated.

Leung and Griffiths [2] first choose the following transformation of field variables: $\omega = P/RT$, $B = 1/RT$ and $\nu_i = \mu_i/RT$, $i = 1, 2$, where R is the gas constant. The fundamental differential relationship is

$$d\omega = \rho_1 d\nu_1 + \rho_2 d\nu - u dB \quad (1)$$

where ρ_i is the molar density of fluid i and u is the internal energy per unit volume. We note that Eq. (1) is easily derived from the expression for the total Gibbs free energy G ,

$$G = N_1 \mu_1 + N_2 \mu_2 = U + PV - TS \quad (2)$$

where N_i is the number of moles of fluid i , U is the total (extensive) internal energy, V is the volume and S is the entropy, together with the differential relationship for a closed system that

$$dG = N_1 d\mu_1 + N_2 d\mu_2 = -S dT + V dP \quad (3)$$

by eliminating the entropy from Eqs. (2) and (3).

Equation (1) is a useful representation since the differentials are of field variables, whereas the conjugate functions are related to *measurable* density variables by

$$\rho = \rho_1 + \rho_2 \quad (4)$$

$$x = \rho_2/(\rho_1 + \rho_2) \quad (5)$$

and the relation for the molar enthalpy h_m ,

$$h_m = \rho^{-1} (P + u) \quad (6)$$

We can thus anticipate that the formalism will yield differential, rather than algebraic equations for the measurable thermodynamic properties.

In the Griffiths and Wheeler formalism [12] one of the field variables, a choice which in principle is arbitrary, is singled out as the "potential" or dependent variable; here the choice for the potential is ω . Leung and Griffiths then introduce a second transformation of independent field variables, ζ , τ and h . These are best understood as *distance* variables and are, respectively, the distance from pure fluid 2, the distance from the critical locus, and the distance from the coexistence surface.

The first new field variable is

$$\zeta = \frac{K_1(B) e^{\nu_1}}{K_2(B) e^{\nu_2} + K_1(B) e^{\nu_1}} = \frac{1}{K(B) e^{\nu_2 - \nu_1} + 1} \quad (7)$$

where $K(B) = K_2(B)/K_1(B)$; it can be interpreted as an activity or fugacity fraction.

This variable is absolutely central to the Leung-Griffiths representation of thermodynamics and in many ways is a field variable analog of the density variable x . In previous publications [2-4,6-8], K was assumed to be a constant with arbitrary value. Here we generalize the model by assuming K can be a temperature dependent function, $K(T)$ or $K(B)$, but must be independent of the chemical potentials, as was first mentioned in Ref. 15.

We first note some important properties of ζ . Our (arbitrary) convention is that $x = 0$ for pure fluid 1 and $x = 1$ for pure fluid 2, the more volatile fluid. In the limit of pure fluid 1, ν_2 has the leading-order divergence

$$\nu_2 \rightarrow \ell \ln x \quad (8)$$

and in the limit of pure fluid 2, ν_1 diverges as

$$\nu_1 \rightarrow \ell \ln (1 - x) = \ell \ln x_1 \quad (9)$$

Therefore, $\zeta = 1$ for $x = 0$ (pure fluid 1) and $\zeta = 0$ for $x = 1$ (pure fluid 2), and at any point within the mixture ζ lies between 0 and 1. Furthermore, for small x , $1 - \zeta$ is proportional to x to leading order and is an analytic function of x , whereas for small $x_1 = 1 - x$, ζ is analytic in, and to leading order proportional to, x_1 .

Had we chosen a different multiplicative factor in the exponent which defines ζ , i.e. [16]

$$\frac{\mu_i}{RT} \longrightarrow \frac{\mu_i Z}{RT} \quad (10)$$

where Z is not an integer (e.g. the inverse critical compressibility factor [16]) then at the respective limits $1 - \zeta$ would be proportional to x^Z and ζ to x_1^Z . While such a redefinition would not by itself be inconsistent, a thermodynamic inconsistency would later arise when ω is expanded in an analytic power series in the redefined ζ , since at the mixture boundaries ω is analytic in x or x_1 . While the Leung–Griffiths formalism can be generalized in other ways, it is important for the above reason not to alter the original definition of ζ .

For well-behaved mixtures and a reasonable choice for $K(B)$, we expect that, as x goes smoothly from 0 to 1, ζ goes smoothly from 1 to 0. The critical locus is defined by the function $P_c(x)$, $T_c(x)$, and $\rho_c(x)$, but these can equally well be viewed as functions of ζ according to the correspondence on the critical locus. The second new field variable introduced by Leung and Griffiths is

$$\tau = \frac{1}{RT_c(\zeta)} - B = B_c(\zeta) - B \quad (11)$$

Note that each successive new field variable is defined in terms of both the old and previously defined new field variables. Here, τ is a measure of distance from the critical line along a locus of constant ζ , and is negative in the two-phase region.

The third new field variable introduced by Leung and Griffiths is

$$\begin{aligned} h &= \ell_n \left[K_1(B) e^{\nu_1} + K_2(B) e^{\nu_2} \right] - \ell_n \left[K_1(B) e^{\nu_1^\sigma} + K_2(B) e^{\nu_2^\sigma} \right] \\ &= \ell_n \left[K_1(B) e^{\nu_1} + K_2(B) e^{\nu_2} \right] - H(\zeta, \tau) \end{aligned} \quad (12)$$

where the superscript σ refers to the value of ν_i on the vapor-liquid coexistence surface for the same (ζ, τ) as the thermodynamic point for which h is being evaluated. The second line of Eq. (12) defines the function $H(\zeta, \tau)$. While ζ and h are first defined in terms of two functions $K_1(B)$ and $K_2(B)$, they only depend on $K = K_2/K_1$, but H as defined above can depend on K_1 and K_2 separately.

The critical line and coexistence surface have a very simple mathematical form in the variable space (ζ, τ, h) ; the critical line is simply the straight line segment $h = 0$, $\tau = 0$, $0 \leq \zeta \leq 1$, and the coexistence surface is the strip $h = 0$, $\tau < 0$, $0 \leq \zeta \leq 1$. Note that $\tau < 0$ on the coexistence surface so that further specification of h is required for $\tau > 0$. Leung and Griffiths state that for $\tau > 0$ the superscript σ refers to the value of ν_1 on the smooth extension of the coexistence surface beyond the critical line, although in practice this extension is a function of the model to be constructed. However, since the primary concern of this work is the VLE surface for which $\tau < 0$, the problem of defining h for $\tau > 0$ is of no immediate consequence.

At this point the partial differential relationships specified by Eq. (1) are related to the partial differential relationships of ω with respect to the new field variables, i.e.

$$\begin{aligned} \left[\frac{\partial \omega}{\partial \nu_1} \right]_{\nu_2, B} &= \rho_1 = \left[\frac{\partial \omega}{\partial \zeta} \right]_{\tau, h} \left[\frac{\partial \zeta}{\partial \nu_1} \right]_{\nu_2, B} + \left[\frac{\partial \omega}{\partial \tau} \right]_{\zeta, h} \left[\frac{\partial \tau}{\partial \nu_1} \right]_{\nu_2, B} \\ &\quad + \left[\frac{\partial \omega}{\partial h} \right]_{\zeta, \tau} \left[\frac{\partial h}{\partial \nu_1} \right]_{\nu_2, B} \end{aligned} \quad (13)$$

and similarly for $\left[\frac{\partial \omega}{\partial \nu_2} \right]_{\nu_1, B} = \rho_2$ and $\left[\frac{\partial \omega}{\partial B} \right]_{\nu_1, \nu_2} = -u$. We eschew the shorthand notation of Leung and Griffiths, e.g. $\omega_\zeta = (\partial \omega / \partial \zeta)_{\tau, h}$, because we shall subsequently eliminate τ in favor of yet another variable t and such shorthand notation could lead to confusion since, for example, $(\partial \omega / \partial \zeta)_{\tau, h} \neq (\partial \omega / \partial \zeta)_{t, h}$.

While the resulting equations in principle can be quite complicated, a remarkable simplification takes place for the total molar density,

$$\rho = \rho_1 + \rho_2 = \left[\frac{\partial \omega}{\partial h} \right]_{\zeta, \tau}, \quad (14)$$

which is a consequence of the following equations,

$$\left[\frac{\partial \zeta}{\partial \nu_1} \right]_{\nu_2, B} + \left[\frac{\partial \zeta}{\partial \nu_2} \right]_{\nu_1, B} = 0 \quad (15)$$

$$\left[\frac{\partial \tau}{\partial \nu_1} \right]_{\nu_2, B} + \left[\frac{\partial \tau}{\partial \nu_2} \right]_{\nu_1, B} = 0 \quad (16)$$

$$\left[\frac{\partial h}{\partial \nu_1} \right]_{\nu_2, B} + \left[\frac{\partial h}{\partial \nu_2} \right]_{\nu_1, B} = 1 \quad (17)$$

Equation (15) is a direct consequence of the fact that ζ is a function only of $(\nu_2 - \nu_1)$. Equation (16) follows from Eq. (11), where B is held constant,

$$\left[\frac{\partial \tau}{\partial \nu_i} \right]_{\nu_j, B} = \frac{dB_c(\zeta)}{d\zeta} \left[\frac{\partial \zeta}{\partial \nu_i} \right]_{\nu_j, B} \quad (18)$$

Finally, because of Eqs. (15) – (16)

$$\left[\frac{\partial H}{\partial \nu_1} \right]_{\nu_2, B} + \left[\frac{\partial H}{\partial \nu_2} \right]_{\nu_1, B} = 0 \quad (19)$$

and Eq. (17) follows directly from Eqs. (12) and (19).

Expressions for the other measurable density variables x and u are somewhat more complicated. For x , we require ρ_2 which is given by Eq. (13) with subscripts 1 and 2 reversed. Since

$$\left[\frac{\partial \zeta}{\partial \nu_2} \right]_{\nu_1, B} = -\zeta (1 - \zeta) \quad (20)$$

and, from Eqs. (12), (18) and (20)

$$\left[\frac{\partial H}{\partial \nu_2} \right]_{\nu_1, B} = 1 - \zeta + \zeta (1 - \zeta) \left[\left[\frac{\partial H}{\partial \zeta} \right]_{\tau} + \frac{dB_c(\zeta)}{d\zeta} \left[\frac{\partial H}{\partial \tau} \right]_{\zeta} \right] \quad (21)$$

it can be shown that

$$x = \rho_2/\rho = 1 - \zeta - \zeta (1 - \zeta) Q/\rho \quad (22)$$

where the function Q is defined by

$$Q = \left[\frac{\partial \omega}{\partial \zeta} \right]_{\tau, h} + \frac{dB_c(\zeta)}{d\zeta} \left[\frac{\partial \omega}{\partial \tau} \right]_{\zeta, h} - \rho \left[\left[\frac{\partial H}{\partial \zeta} \right]_{\tau} + \frac{dB_c(\zeta)}{d\zeta} \left[\frac{\partial H}{\partial \tau} \right]_{\zeta} \right] \quad (23)$$

Two important observations are emphasized at this point. First, since ρ_1 and ρ_2 , or ρ and x , involve only partial derivatives with B (or T) held constant, their formal expressions are unchanged when K , which appears in the definition of ζ , is generalized from a constant to a temperature-dependent function. However, the formal expression for the energy density will be changed, as discussed below.

Second, from Eq. (20) the partial derivatives of ζ required to calculate x are algebraic functions of ζ itself. This would not be true in general, since transformation to an arbitrary function of μ_1 , μ_2 , T and parameters (e.g. K) would lead, through the analogs of Eq. (13), to partial derivatives that could depend *differently* on μ_1 , μ_2 , T and K . This property of ζ is reminiscent of similar properties of the Fermi-Dirac distribution function [17], which ζ closely resembles.

Only because of this property, knowledge of K will turn out to be unnecessary for calculation of the P - T - ρ - x coexistence surface. It is evident already that if we can "model", i.e. hypothesize, forms for ω at $h = 0$ and H as functions of ζ and τ , as well as the critical properties as functions of ζ and the leading-order dependence of ω on h , then ρ and x can be calculated explicitly without knowledge of K . Since field variables are continuous functions of each other but have discontinuous derivatives at a phase boundary, Eq. (14) will yield a liquid or vapor density according as h approaches zero from above or below. Substitution of these densities into Eqs. (22) and (23) will yield respectively the liquid and vapor compositions.

We next examine the internal energy density u . The analog of Eq. (13) is

$$\begin{aligned} -u = \left[\frac{\partial \omega}{\partial B} \right]_{\nu_1, \nu_2} &= \left[\frac{\partial \omega}{\partial \zeta} \right]_{\tau, h} \left[\frac{\partial \zeta}{\partial B} \right]_{\nu_1, \nu_2} + \left[\frac{\partial \omega}{\partial \tau} \right]_{\zeta, h} \left[\frac{\partial \tau}{\partial B} \right]_{\nu_1, \nu_2} \\ &+ \left[\frac{\partial \omega}{\partial h} \right]_{\zeta, \tau} \left[\frac{\partial h}{\partial B} \right]_{\nu_1, \nu_2} . \end{aligned} \quad (24)$$

Furthermore, from Eq. (7),

$$\left[\frac{\partial \zeta}{\partial B} \right]_{\nu_1, \nu_2} = -\zeta (1 - \zeta) \frac{d}{dB} \ell_n K . \quad (25)$$

$$\left[\frac{\partial \tau}{\partial B} \right]_{\nu_1, \nu_2} = -1 - \frac{dB_c(\zeta)}{d\zeta} \zeta (1 - \zeta) \frac{d}{dB} \ell_n K . \quad (26)$$

These terms were simply zero and minus one, respectively, in previous derivations where K was held constant. In addition,

$$\begin{aligned} \left[\frac{\partial h}{\partial B} \right]_{\nu_1, \nu_2} &= \left[\frac{\partial H}{\partial \tau} \right]_{\zeta} + \frac{d}{dB} \ell_n K \left\{ 1 - \zeta + \zeta (1 - \zeta) \left[\left[\frac{\partial H}{\partial \zeta} \right]_{\tau} + \frac{dB_c(\zeta)}{d\zeta} \left[\frac{\partial H}{\partial \tau} \right]_{\zeta} \right] \right\} \\ &+ \frac{d}{dB} \ell_n K_1 \end{aligned} \quad (27)$$

Combining these results, we find that

$$u = \left[\frac{\partial \omega}{\partial \tau} \right]_{\zeta, h} - \rho \left[\frac{\partial H}{\partial \tau} \right]_{\zeta} - \rho_1 \frac{d}{dB} \ell_n K_1 - \rho_2 \frac{d}{dB} \ell_n K_2 \quad (28)$$

which reproduces Eq. (2.20) of Leung and Griffiths except, of course, for the last two additional terms. Equation (28) can be differentiated to obtain the specific heats, as described for the special case of a pure fluid in App. B.

An interesting connection can now be made with the reference states of the chemical potentials. It is well known that the zeroes of chemical potential are arbitrary, and the transformations $\mu_1 \rightarrow \mu_1 + \mu_{10}$ and $\mu_2 \rightarrow \mu_2 + \mu_{20}$, are constant over all thermodynamic space, leave the equation of state $P(\rho, T, x)$ unchanged. However, the internal energy density is shifted by $(\rho_1 \mu_{10} + \rho_2 \mu_{20})$. From Eqs. (7) and (12), such a shift can be effected without altering ζ or h , if K_1 is simultaneously multiplied by $e^{-B\mu_{10}}$ and K_2 by $e^{-B\mu_{20}}$. Then under such a shift, Eq. (28) yields precisely the required shift in u , whereas the expressions for ρ and x are appropriately left unchanged.

Therefore, the temperature dependence of K absorbs the degrees of freedom present in the reference states for μ_1 and μ_2 , but also introduces additional degrees of freedom to the model. As an aside, in an earlier paper [6] it was incorrectly implied that such a shift in zeroes is equivalent to a change in K from one constant to another. Rather, such a shift would make a constant K become temperature-dependent.

At this point, for the first time in our discussions we come to a distinction between the "original" and "modified" Leung-Griffiths formalisms, as contrasted in App. C. In the latter version, first introduced by Moldover and Gallagher [3,4], the variable τ is eliminated in favor of t , where

$$t = \frac{T - T_c(\zeta)}{T_c(\zeta)} = \frac{\tau}{B_c(\zeta) - \tau} \quad (29)$$

A disadvantage of the variable τ is that it is not dimensionless. While it could be made dimensionless [16] by multiplication by RT_{c1} or RT_{c2} , where T_{ci} is the critical temperature of pure fluid i , such a redefinition would destroy the symmetry of the model between the labels of two fluids. The variable t is conveniently both dimensionless and symmetric in the fluid labels. Partial derivatives then transform as follows:

$$\left[\frac{\partial \omega}{\partial \tau} \right]_{\zeta, h} = \left[\frac{\partial \omega}{\partial t} \right]_{\zeta, h} \frac{t + t^2}{\tau} \quad (30)$$

$$\left[\frac{\partial \omega}{\partial \zeta} \right]_{\tau, h} = \left[\frac{\partial \omega}{\partial \zeta} \right]_{t, h} - \frac{t^2}{\tau} \frac{dB_c(\zeta)}{d\zeta} \left[\frac{\partial \omega}{\partial t} \right]_{\zeta, h} \quad (31)$$

and partial derivatives of ω with respect to h are unchanged.

The modified version also introduces a function \bar{Q} , the first two terms of Eq. (23).

$$\begin{aligned}
\bar{Q} &= \left[\frac{\partial \omega}{\partial \zeta} \right]_{\tau, h} + \frac{dB_c(\zeta)}{d\zeta} \left[\frac{\partial \omega}{\partial \tau} \right]_{\zeta, h} \\
&= \left[\frac{\partial \omega}{\partial \zeta} \right]_{t, h} + \frac{t}{\tau} \frac{dB_c(\zeta)}{d\zeta} \left[\frac{\partial \omega}{\partial t} \right]_{\zeta, h} \\
&= \left[\frac{\partial \omega}{\partial \zeta} \right]_{t, h} + \frac{1}{B_c(\zeta)} \frac{dB_c(\zeta)}{d\zeta} (1+t) \left[\frac{\partial \omega}{\partial t} \right]_{\zeta, h}
\end{aligned} \tag{32}$$

and Eq. (22) is rewritten as

$$x = 1 - \zeta - \zeta (1 - \zeta) \left[\frac{\bar{Q}(\zeta, t)}{\rho} - \frac{\bar{Q}(\zeta, t=0)}{\rho_c(\zeta)} - \bar{H}(\zeta, t) \right] \tag{33}$$

where the function \bar{H} is defined by

$$\bar{H}(\zeta, t) = \left[\frac{\partial H}{\partial \zeta} \right]_{\tau} + \frac{dB_c(\zeta)}{d\zeta} \left[\frac{\partial H}{\partial \tau} \right]_{\zeta} - \frac{\bar{Q}(\zeta, t=0)}{\rho_c(\zeta)} \tag{34}$$

The addition and subtraction performed in the construction of Eqs. (33) – (34) isolates those terms which cause x to deviate from $(1-\zeta)$ along the critical line. In previous work [3,4,6–8], the hypothesis that $x = 1 - \zeta$ along the critical locus was employed, but it was assumed that this was an approximate relation that could never be made exact. However, with our present generalization of the model to admit a temperature-dependent K , we can make a stronger statement. A rearrangement of Eq. (7) gives

$$\ln K = (\mu_1 - \mu_2)/RT + 2 \tanh^{-1} (1 - 2\zeta) \tag{35}$$

Let us consider the consequences of assuming $x = 1 - \zeta$ on the critical locus, in which case Eq. (35) becomes

$$\ln K = (\mu_1 - \mu_2)/RT + 2 \tanh^{-1} (2x - 1) \tag{36}$$

On the interval $[0,1]$ in x , each term on the right-hand side is smooth and finite except for singularities at the boundaries. However, from Eqs. (8) and (9) these singularities cancel, and the full expression is always finite.

Let us further consider a mixture for which T_c is a monotonic function of x . This restriction includes most normal mixtures but excludes most azeotropic ones. Again, it is emphasized that the chemical potentials along the critical line, except for their dilute-limit singularities, must be regarded as unknown. However, at each temperature between the critical temperatures of the two pure fluids, the right-hand side of Eq. (36) has a particular, finite value. If we set $\ln K$ equal to this value, we have constructed a temperature-dependent K such that $x = 1 - \zeta$ on the critical locus *exactly*.

While we cannot determine this particular $K(T)$ quantitatively, we can exploit the knowledge that it exists and, once the zeroes of chemical potential have been specified, is unique. On primarily empirical grounds, we have found that this particular choice of $K(T)$ appears to be optimal for correlation of VLE data for the majority of mixtures. This choice imposes the constraint in Eq. (34) that $\bar{H}(\zeta, 0) = 0$, as seen from Eq. (33). The same general argument can apply to any smooth function $x_c(\zeta)$ that satisfies the boundary conditions $x_c(0) = 1$ and $x_c(1) = 0$, although forms that deviate too much from linearity will probably violate stability criteria [12].

For most azeotropic mixtures, T_c has a minimum in x , and thus over a certain interval two distinct compositions possess the same critical temperature. Consequently, in general a $K(T)$ does not exist such that $x = 1 - \zeta$ for the entire critical locus. However, in view of the success in applying earlier versions of this model to azeotropic mixtures, it can be presumed that ζ can still be made approximately linear in x along the critical locus for such mixtures.

3. Specification of the Thermodynamic Potential

The preceding section has described the definition of a new set of thermodynamic variables and the conversion of the basic laws of thermodynamics into relationships among these new variables. As a consequence, the equations derived there are perfectly general and are independent of any particular assumptions or approximations.

To proceed, we now construct an explicit mathematical form for ω as a function of ζ , t and h . This step is analogous to the imposition of an equation of state $P(T, \rho, x)$ in the conventional thermodynamic formalism. Here $\omega(\zeta, t, h)$ is a "generalized equation of state" in terms of field variables, in contrast to the conventional mixed set of field and density variables.

The development in this section follows that of Moldover and Gallagher [4], which is a slight modification of that of Leung and Griffiths [2]. For the steps described in this section, we have essentially left the Moldover–Gallagher formalism intact in the current version of the model. However, changes and additional features should prove to be useful in future work, and such possible changes are discussed where appropriate.

We first take note of two important boundary conditions that the generalized equation must satisfy. For $h = 0$ and $\zeta = 0$ or $\zeta = 1$, the equation must reduce to that of the vapor pressure equation for pure fluid 1 or 2 respectively, which may be conveniently represented as

$$\omega_{\text{pure}} = \frac{P}{RT} = \frac{P_c}{RT_c} \left[1 + C_3 (-t)^{2-\alpha} + C_4 t + C_5 t^2 + C_6 t^3 \right] \quad (37)$$

where the C_i are dimensionless constants that are characteristic of the particular pure fluid.

Equation (37) introduces the critical exponent α , which is defined as the exponent characterizing the divergence of the specific heat at constant volume C_v , i.e. in the asymptotic limit near the critical point,

$$C_v \propto t^{-\alpha} \quad (38)$$

The connection between Eqs. (37) and (38) is derived in App. B. The exponent α has a theoretical value of 0.110 largely confirmed by experiment [18], but for an "effective" exponent providing a best fit over an extended critical region we shall use $\alpha = 0.1$. Classical equations of state (see App. A) yield the result $\alpha = 0$, i.e. no divergence in C_v .

In addition, for $\zeta = 0$ or 1 the coexisting densities should reduce to an appropriate form for a pure fluid; a convenient such form is

$$\rho_{\text{pure}} = \rho_c \left[1 \pm C_1 (-t)^\beta + C_2 t \right] \quad (39)$$

where $\rho_{\text{pure}} = (\partial\omega/\partial h)_{\zeta, t}$ evaluated at $h=0$ and $\zeta=0$ or 1 , and the plus sign refers to the saturated liquid and the minus to the saturated vapor.

Equation (39) introduces a second critical exponent β , which has a theoretical value of 0.325 also confirmed by experiment [19], but as an "effective" exponent over an extended critical region is best represented by 0.355 . Classical equations of state yield the result $\beta = 0.5$, a significant difference which in our view is largely responsible for the deficiencies of such classical equations.

In the study of critical phenomena, a large number of critical exponents were originally introduced. However, according to Widom's scaling hypothesis [20], only two of these exponents are independent, and fixing the values of two exponents determines all other exponents. Here we take the independent exponents to be α and β .

Both Eqs. (37) and (39) are approximations which, for pure fluids, leave something to be desired, although they should be adequate for our generalization to mixtures over an extended critical region where the experimental data are typically less precise. In practice, the vapor pressure curve is more efficiently fitted by an Antoine equation [21], or a representation that combines an Antoine equation with the necessary asymptotic expansion, e.g.

$$\ln \left[\frac{P}{P_c} \right] = A_1 \left[1 - \frac{T_c}{T} \right] + A_2 (-t)^{2-\alpha} + A_3 t + A_4 t^2 + \dots \quad (40)$$

where the A_i are relatively small for $i \geq 2$. The $(-t)^{2-\alpha}$ term is not typically required from a statistical analysis of vapor pressure data; in fact some correlators [22], on empirical grounds, prefer in Eq. (40) an exponent near 1.3 instead of $1.9 = 2-\alpha$. While Eq. (40) is a more efficient representation of the vapor pressure curve than Eq. (37), we do not know of a mechanism to incorporate Eq. (40) into a scaling-law formalism, and here Eq. (37) has been used instead.

More importantly, Eq. (39) is representative of so-called "simple scaling", whereas current theoretical models employ so-called "revised [23] and extended [24] scaling". Simple scaling is characterized by a single non-analytic term (with coefficient C_1) for the vapor-liquid density difference, and a linear rectilinear diameter from the term with C_2 . In revised scaling [23], the rectilinear diameter possesses a "hook" near the critical point, and in extended scaling, as first introduced by Wegner [24], there is a second term in Eq. (39), proportional to $(-t)^{\beta\Delta}$ with $\Delta \approx 0.5$, with opposite signs for liquid and vapor.

Incorporation of revised and/or extended scaling would considerably increase the complexity of the expressions for $\omega(\zeta, t, h)$. Almost certainly, as discussed in App. C, revised scaling will be required for a proper description of the supercritical one-phase region, $h \neq 0$. Furthermore, as will be discussed in the propane + n-octane correlation in Part II of this series, extended scaling may well be the next feature introduced for VLE within the evolution of the present model. However, for a wide range of mixtures the VLE surface is accurately represented by simple scaling, so revised scaling and extended scaling are not at present necessary for the formalism.

Equations (37) and (39) can be rearranged as expressions written entirely in terms of reduced units, i.e. thermodynamic variables divided by their critical values. If the principle of corresponding states were obeyed exactly, i.e. if all fluids were "conformal", C_i , $i = 1 \dots 6$, would be universal constants, the same for all pure fluids. In fact, the C_i are nearly constant from fluid to fluid except for C_2 , the slope of the rectilinear diameter, and C_6 , the coefficient of the final term in a truncated polynomial series. (The helium isotopes, probably because of residual quantum effects, are an exception to this rule.) As the molecules become more acentric, the vapor pressure curve becomes steeper at the critical point, and, as a result, fluids of highly acentric molecules [4] possess a larger value of C_4 .

We require an explicit mathematical representation for the thermodynamic potential consistent with the behavior postulated by Griffiths and Wheeler [12] near critical. In particular, the potential must be a continuous function of the independent field variables, but must have appropriately discontinuous derivatives, cf. Eq. (14). Furthermore, the magnitude of the discontinuity must vary with distance from critical (i.e., $|t|$) according to the appropriate critical exponent.

To accomplish this, we follow Moldover and Gallagher [4] and utilize the Schofield linear model [25]. For present purposes, the Schofield model may be regarded simply as a mathematical device to construct a continuous function with discontinuous derivatives. While other such constructions exist, the Schofield model is particularly convenient in that the critical exponents can be chosen at will. Yet another transformation (our last one) from t and h to new variables r and θ is required. An analytic background component in the untransformed variables can be added to this singular function, thereby changing the overall thermodynamics but not changing the essential structure of the phase transition surface.

Given Eqs. (37) and (39) as boundary conditions, the thermodynamic potential is thus written as the sum of an analytic potential and a singular potential,

$$\omega(\zeta, t, h) = \omega_{\text{an}}(\zeta, t, h) + \omega_{\text{sing}}(\zeta, t, h), \quad (41)$$

where the two terms of Eq. (41) generate, respectively, the analytic and nonanalytic terms of Eqs. (37) and (39). The functional form for the analytic part of the potential is

$$\begin{aligned} \omega_{\text{an}}(\zeta, t, h) = & \frac{P_c(\zeta)}{RT_c(\zeta)} \left[1 + C_4(\zeta) t + C_5(\zeta) t^2 + C_6(\zeta) t^3 \right] \\ & + \rho_c(\zeta) \left[1 + C_2(\zeta) t \right] h \end{aligned} \quad (42)$$

where $P_c(\zeta)$, $T_c(\zeta)$ and $\rho_c(\zeta)$ are the critical pressure, temperature and density for a mixture with composition x corresponding to the given value of ζ on the critical line, as discussed in the previous section. At this point in the development, $C_i(\zeta)$ can be any function of ζ which satisfies the boundary conditions

$$C_i(0) = C_i^{(2)} \quad (43)$$

$$C_i(1) = C_i^{(1)} \quad (44)$$

where $C_i^{(1)}$ and $C_i^{(2)}$ are the coefficients in Eqs. (37) and (39) for pure fluids 1 and 2 respectively, in which case the correct pure-fluid limits are clearly attained.

It is worth noting that we could add terms proportional to h^2 , h^3 , etc. to Eq. (42) and the coexistence surface would not be changed. However, such terms would change the thermodynamic behavior in the one-phase region. For the study of one-phase thermodynamics, which is beyond the scope of the present work, this is a useful degree of freedom within the Leung-Griffiths model; different thermodynamic potentials can be constructed which lead to different one-phase equations of state but the same VLE surface.

For the singular potential, we transform t and h to two new variables r and θ . At the critical point $r = 0$, and r is (crudely speaking) a measure of distance from the critical point. On the coexistence surface, $\theta = 1$ on the liquid side and $\theta = -1$ on the vapor side, while $\theta = 0$ is approximately the one-phase critical isochore (see App. B).

Here r and θ somewhat resemble a polar coordinate system with the critical point at the origin, although loci of constant r are not circular on a P - T plot. The discontinuity in $\rho = (\partial\omega/\partial h)_{\zeta, t}$ at the coexistence surface is introduced by the discontinuous jump in θ for $+1$ to -1 as the coexistence surface is crossed, whereas ω_{sing} , t and h are smooth functions of r and θ .

The particular transformation and parametric representation of ω_{sing} is as follows [4]:

$$t = \frac{r(1-b^2 \theta^2)}{b^2 - 1} \quad (45)$$

$$h = \frac{P_c(\zeta)}{R T_c(\zeta)} \frac{C_3(\zeta)}{\rho_c(\zeta) C_1(\zeta) a_T} r^{2-\alpha-\beta} \theta (1 - \theta^2) \quad (46)$$

$$\omega_{\text{sing}}(r, \theta, \zeta) = \frac{P_c(\zeta) C_3(\zeta)}{R T_c(\zeta) a_T} r^{2-\alpha} \left[a_0 + a_2 \theta^2 + a_4 \theta^4 \right] \quad (47)$$

where $C_1(\zeta)$ and $C_3(\zeta)$, at this point in the development, can be any functions of ζ which satisfy the boundary conditions of Eqs. (43)–(44). Note that on the coexistence surface $\theta = \pm 1$, we have $t = -r$, $h = 0$ and ω_{sing} reduces to the term proportional to C_3 in Eq. (37), since, by definition,

$$a_T = a_0 + a_2 + a_4 \quad (48)$$

The parameters b and a_i have yet to be specified. Following Moldover and Gallagher [4], we employ the so-called "restricted Schofield model" in which the parameters are functions of the critical exponents [26]. As stated previously, there are only two independent critical exponents, which have been taken as α and β . Two other important critical exponents are γ , which characterizes the critical divergence of the specific heat at constant pressure

$$C_p \propto t^{-\gamma} \quad (49)$$

and δ , which characterizes the asymptotic behavior of the density and chemical potential of a pure fluid,

$$\mu - \mu_c \propto (\rho - \rho_c)^\delta \quad (50)$$

According to the scaling-law hypothesis [20]

$$\gamma = 2 - \alpha - 2\beta \quad (51)$$

and

$$\delta = 1 + \gamma/\beta \quad (52)$$

With our choice of critical exponents ($\alpha = 0.1$, $\beta = 0.355$), the consistent values for the above critical exponents are $\gamma = 1.19$ and $\delta = 4.3521$.

Within the restricted Schofield model,

$$b^2 = \frac{\delta - 3}{(\delta - 1)(1 - 2\beta)} \quad (53)$$

where, for our choice of critical exponents, $b^2 = 1.3909$. The coefficients a_i are expressed below both algebraically in terms of the critical exponents and numerically for the choices $\alpha = 0.1$ and $\beta = 0.355$

$$a_0 = \frac{\beta\delta - 3\beta - b^2\alpha\gamma}{2b^4(2-\alpha)(1-\alpha)\alpha} = 0.4753 \quad (54)$$

$$a_2 = -\frac{\beta\delta - 3\beta - b^2\alpha(2\beta\delta - 1)}{2b^2(1-\alpha)\alpha} = -0.7561 \quad (55)$$

$$a_4 = \frac{2\beta\delta - 3}{2\alpha} = 0.45 \quad (56)$$

$$a_T = a_0 + a_2 + a_4 = \frac{(b^2 - 1)\beta(1 - 2\beta)}{b^2(2 - \alpha)(1 - \alpha)\alpha} = 0.1692 \quad (57)$$

These terms were given only numerically in Appendix A of Moldover and Gallagher [4].

The singular term in density is obtained from the ratio of Jacobians

$$\left[\frac{\partial \omega_{\text{sing}}}{\partial h} \right]_{t, \zeta} = \frac{\partial(\omega_{\text{sing}, t}) / \partial(r, \theta)}{\partial(h, t) / \partial(r, \theta)} \quad (58)$$

Evaluation of this expression for $\theta = \pm 1$ yields

$$\left[\frac{\partial \omega_{\text{sing}}}{\partial h} \right]_{t, \zeta} = \rho_c(\zeta) C_1(\zeta) r^\beta \theta \left[\frac{(2-\alpha)b^2 a_T + (1-b^2)(a_2 + 2a_4)}{b^2 - 1} \right] \quad (59)$$

Finally, although the algebra is tedious, it can be shown from Eqs. (51)–(57) that the expression in brackets is unity. Thus, from Eqs. (42) and (59), the coexisting densities on a locus of constant ζ are given by

$$\rho(\zeta, t) = \rho_c(\zeta) \left[1 \pm C_1(\zeta) (-t)^\beta + C_2(\zeta) t \right], \quad (60)$$

i.e. the generalization of Eq. (39), where the plus sign refers to the liquid ($\theta = 1$) and the minus sign to the vapor ($\theta = -1$). The full potential for $h = 0$ is the generalization of Eq. (37),

$$\omega(\zeta, t, h = 0) = \frac{P_c(\zeta)}{RT_c(\zeta)} \left[1 + C_3(\zeta) (-t)^{2-\alpha} + C_4(\zeta) t + C_5(\zeta) t^2 + C_6(\zeta) t^3 \right] \quad (61)$$

This completes the generic construction of a continuous potential with discontinuous derivatives. The development has followed very closely that of a pure fluid, with ζ playing the role of a "spectator" variable. We expect that revised scaling [23], where t is replaced by $t + qh$, with q a mixing parameter, or extended scaling [24] could be included similarly with ζ playing a similar spectator role. The explicit mathematics has yet to be constructed and tested, however.

4. Specification of the Functions $C_i(\zeta)$

In the preceding section, we have constructed a thermodynamic potential expanded about $t = 0$ with phase transition properties consistent with the postulates of Griffiths and Wheeler [12]. Within the simplifications of simple scaling and the restricted Schofield

linear model, as well as the truncation of the analytic component at the cubic level in t , the potential is still perfectly general.

This point in the development reaches a limit, beyond which further specification of the model cannot be based on well-established scientific principles. The basic laws of thermodynamics have been incorporated in Sec. 2, and modern understanding of critical behavior, in simplified form, has been incorporated in Sec. 3. In the absence of a microscopic theory which might predict nonuniversal amplitudes about the critical locus from an intermolecular potential, further specification of the model must necessarily be largely empirical.

One possible strategy at this juncture is to allow all parameters and functions as yet undetermined to be adjustable, and to fit them to the VLE data. Thus the $C_i(\zeta)$ could be written as truncated polynomials in ζ (consistent with Eqs. (43) and (44) as boundary conditions), x on the critical locus could also be written as a truncated polynomial in ζ , and the functions $H(\zeta, t)$ or $\bar{H}(\zeta, t)$ could be similarly expanded. Apart from certain details (see App. C), this is the strategy employed within the "original" (as opposed to our "modified") Leung-Griffiths formalism [2,27,28].

The problem with such a strategy is the extreme redundancy in the resulting mathematical description. As previously noted, K can be any constant or, within limits, any temperature-dependent function. Thus there is in principle an infinite set of Leung-Griffiths models with different explicit parameter values but which are equivalent in describing a particular coexistence surface. Such redundancy can be expected to make convergence of a calculational algorithm extremely problematical. Furthermore, it is hard to develop an intuition as to what effect the change of a particular parameter has on the symbolized VLE surface, or to develop guidelines for the points of truncation of the polynomials. Therefore, it is appropriate to search for hypotheses which further narrow down the model, even if such hypotheses have only empirical justifications.

The first hypothesis, central to the reformulation of the Leung and Griffiths model, was originally introduced by Moldover and Gallagher [3,4] and states that the functions $C_i(\zeta)$ are linear in ζ , i.e.

$$C_i(\zeta) = C_i^{(2)} + \zeta C_i' \quad (62)$$

$$C_i' = C_i^{(1)} - C_i^{(2)} \quad (63)$$

In our most general model to date we shall retain these restrictions for $i = 3, \dots 6$ but *not* for $i = 1$ or 2 .

The above hypothesis represents a highly idealized assumption of the smoothness of the coexistence surface in P - T - ζ space. As explained earlier, if the principle of corresponding states were obeyed exactly, the C_i would be universal constants for all pure fluids. The linear interpolation of Eqs. (62) – (63) thus implies that C_i is typically close to constant for all ζ , $0 \leq \zeta \leq 1$. In fact, our essential phenomenological concept is that the thermodynamic behavior of the mixture along lines of constant ζ closely resembles that of a pure fluid, as was somewhat implied in the previous section. Loci of constant ζ in our model, on a P - T graph, have essentially the same shape as, and are parallel to, the pure-fluid vapor pressure curves. Similarly, lines of constant t have essentially the same shape as, and are parallel to, the critical line. This is illustrated explicitly in Fig. 5. It has recently been demonstrated that such an idea is useful for the prediction of interfacial tension of mixtures [29], as well as for phase equilibrium.

We can anticipate some instances where our assumptions of ideal smoothness in P - T - ζ space will clearly break down. For "Type 2" mixtures in the van Konynenberg–Scott classification scheme [9], the phase diagram includes liquid–liquid equilibrium (LLE) in addition to VLE, and an LLE critical locus or locus of "consolute points" distinct from the VLE critical locus of "plait points". This second critical locus joins the VLE surface at a critical end point, and the LLE coexistence surface joins the VLE coexistence surface at a three-phase locus [11].

From the "180° rule" [30], the VLE coexistence surface, $\omega(\zeta, t, h = 0)$, must have a "crease" or discontinuity in $\partial\omega/\partial\zeta$ at the three-phase locus. Such a discontinuity will end at the critical end point, but will likely propagate beyond as a continuous but highly curved ridge in the $h = 0$ surface, and could greatly distort the shape of the surface compared to its form in the absence of LLE.

Henceforth we shall assume that the mixture under consideration either displays no LLE, or has a locus of consolute points at temperatures well below the critical temperature of the more volatile component. Specific guidelines for the temperature interval have yet to be established. While liquid–liquid immiscibility has not been observed in carbon dioxide + methane, that mixture has a freezing surface which comes very close to the locus of plait points [31], and we have found evidence that the mixture, if it did not freeze, would separate into two immiscible liquid phases not far below the critical temperature of

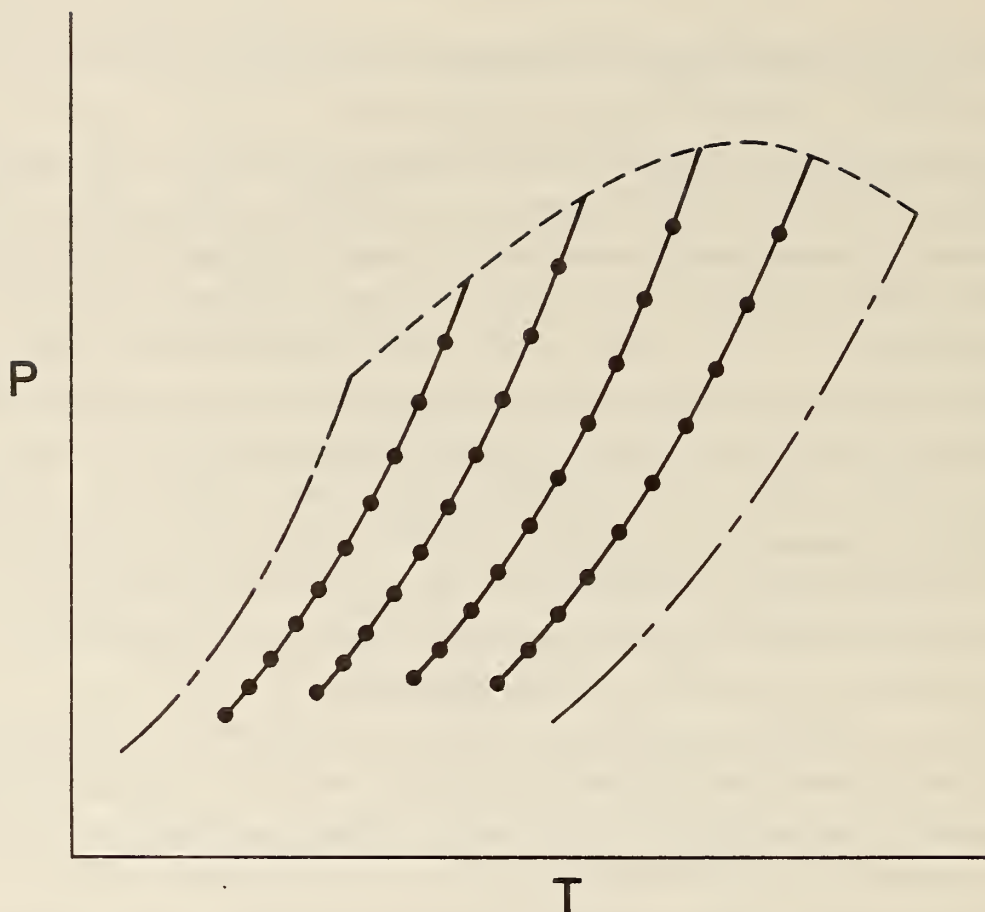


Figure 5. Loci of constant ζ in the P - T plane (schematic). The broken curves are the pure-fluid vapor pressure curves, the dashed curve is the critical locus, and the solid curves are loci of constant ζ at, for example, $\zeta = 0.2, 0.4, 0.6$, and 0.8 from left to right. The dots denote even intervals of, for example, 0.02 in t along loci of constant ζ .

methane. This probably explains why our model has failed to correlate carbon dioxide + methane, as first noted by Al-Sahhaf et al. [32] and as explained more fully in Part II of this series.

The change in density across the phase boundary is, from Eq. (60)

$$\Delta\rho = \rho_\ell - \rho_v = 2C_1(\zeta)(-t)^\beta \rho_c(\zeta) \quad (64)$$

where the subscripts ℓ and v refer to liquid and vapor, respectively. The change in composition across the phase boundary, from Eq. (33), is

$$\Delta x = [x_\ell - x_v] = \zeta(1 - \zeta) [\bar{Q}(\zeta, t)] (\rho_v^{-1} - \rho_\ell^{-1}) \quad (65)$$

Onuki [33] has introduced the two functions

$$\alpha_1 = R^{-1} \Delta s / (\Delta\rho / \rho_c) \quad (66)$$

$$\alpha_2 = \Delta x / (\Delta\rho / \rho_c) \quad (67)$$

where Δs is the molar entropy difference between liquid and vapor. While these functions could have meaning at any two-phase point, we are concerned here with their limiting values at the critical locus, i.e. $t = 0$. Since Δs and Δx asymptotically approach the critical locus as $(-t)^\beta$, the limits are finite. Also, the limits are the same for any thermodynamic path not parallel to the critical locus [12].

Obviously, for normal mixtures α_2 is zero at the two pure-fluid boundaries, and has a single extremum typically near $x = 0.5$. The sign of α_2 depends on the arbitrary convention employed for composition; for ours, it is negative for normal mixtures. In the case of azeotropic mixtures, α_2 is zero at the azeotrope and has two extrema, one between each of the pure fluids and the azeotrope.

We shall refer to α_2 as the "distance from azeotropy". Onuki [33] calls it the "degree of azeotropy", but his terminology is in our view less satisfactory, first because in customary usage a given mixture either is or is not azeotropic, and second because a larger

absolute value of α_2 denotes a state further from, not closer to, azeotropic behavior. The concept is somewhat similar to "relative volatility", except that in customary usage relative volatility is reserved for the function

$$\alpha_{12} = x_\ell (1 - x_v) / [x_v (1 - x_\ell)]$$

which approaches unity at the mixture critical point.

Another useful concept is α_{2m} , which we call the "maximum distance from azeotropy",

$$\alpha_{2m} = \max |\alpha_2| \quad (68)$$

Whereas relative volatility is a property of a particular two-phase state or (P,T) point of a given mixture, distance from azeotropy, or α_2 at critical, is a property of a particular mixture and composition, and maximum distance from azeotropy is a property of the mixture as a whole, as well as a measure of dissimilarity of the two pure fluids.

We alluded in the introduction to a quantitative measure for the difficulty of fitting a particular mixture. In fact, α_{2m} is precisely this quantitative measure. Within our model most parameters will be determined from fits to experimental pure fluid coexistence surfaces or the critical locus, but a limited number of additional parameters will be needed. Based on our analysis of the highest quality VLE data, we have developed guidelines within which only certain of the parameters may be used for a given mixture according to the value of α_{2m} . In only the most ideal cases (very small α_{2m}), there are no adjustable parameters and our model reduces to that of Moldover and Gallagher [3,4], in which the coexistence surface is *determined* from the pure fluid coexistence properties and the critical locus. As α_{2m} increases, more parameters become necessary.

From Eqs. (32), (64), (65) and (67), at the critical locus,

$$\begin{aligned} \alpha_2 &= \rho_c^{-1} \zeta (1 - \zeta) \bar{Q}(\zeta, t=0) \\ &= (R\rho_c)^{-1} \zeta (1 - \zeta) \left\{ \frac{d}{d\zeta} \left[\frac{P_c}{T_c} \right] + \left[\frac{d}{d\zeta} \left[\frac{1}{T_c} \right] \right] \left[T_c \left[\frac{\partial P}{\partial T} \right]_{\zeta, t=0} - P_c \right] \right\} \end{aligned} \quad (69)$$

$$= (R\rho_c)^{-1} \zeta (1 - \zeta) \frac{dx}{d\zeta} \left\{ \frac{d}{dx} \left[\frac{P_c}{T_c} \right] + \left[\frac{d}{dx} \left[\frac{1}{T_c} \right] \right] \left[T_c \left[\frac{\partial P}{\partial T} \right]_{\zeta, t=0} - P_c \right] \right\}$$

Equation (69) is a thermodynamic identity, not based on any approximations. Also, both α_2 and the above composition derivatives of critical properties are experimentally measurable. For example, from isothermal VLE data $\alpha_2 = \rho_c (\partial x / \partial \rho)_T$ and hence can be determined from the slope at the critical point of isotherms on diagrams such as Fig. 4.

One can also determine α_2 from VLE data along isopleths. With an argument similar to those used by Wheeler et al. [34] to resolve an apparent paradox concerning mixture compressibility, and by Levelt Sengers [35] to derive the slope of the so-called "bird's beak" isotherm at $T = T_{c2}$, we may write

$$\left[\frac{\partial \rho}{\partial T} \right]_{\text{CRL}} = \left[\frac{\partial \rho}{\partial T} \right]_{x, \text{CXS}}^c + \left[\frac{\partial \rho}{\partial x} \right]_{T, \text{CXS}}^c \left[\frac{\partial x}{\partial T} \right]_{\text{CRL}} \quad (70)$$

where, following the notation of Ref. 34, CRL denotes the critical line and CXS the coexistence surface, and the superscript c denotes evaluation at the critical point. The first factor of the second term is, from above, equal to ρ_c / α_2 , and therefore

$$\alpha_2 = \frac{\rho_c dx_c / dT_c}{\frac{d\rho_c}{dT_c} - \left[\frac{\partial \rho}{\partial T} \right]_{x, \text{CXS}}^c} \quad (71)$$

where all quantities on the right-hand side are measurable and the second term in the denominator is the inverse slope of the isopleth at the critical point, cf. Fig. 2. Note that for a pure fluid or an azeotrope the second term in the denominator becomes infinite, so $\alpha_2 \rightarrow 0$.

As shown in Sec. 3, if $T_c(x)$ is monotonic there exists a $K(T)$ such that $x = 1 - \zeta$ on critical. In this case, the only expression not ordinarily measurable in Eq. (69) is $(\partial P / \partial T)_{\zeta, t=0}$, the slope of the constant- ζ locus at the critical point, and within our model

$$\alpha_2 = -(R\rho_c)^{-1} x (1 - x) \left[\frac{d}{dx} \left[\frac{P_c}{T_c} \right] + C_4 P_c \frac{d}{dx} \left[\frac{1}{T_c} \right] \right] \quad (72)$$

Empirical principle: If for a given Type 1 mixture of nonpolar fluids α_2 is calculated from Eq. (72) with a linearly interpolated $C_4(x)$, and $\alpha_{2m} \leq 0.25$, then Eqs. (62) – (63) are valid for $i = 3, \dots, 6$ and the (unique) choice of $K(T)$ such that $x = 1 - \zeta$ along critical.

We do not assert that the above principle is in any sense exact, or that an experiment specifically designed to observe deviations from it might not locate some. However, from extensive experience in VLE correlations we do claim that such a principle leads to quantitatively successful fits of the highest quality VLE data presently available.

We have therefore found a very useful and important empirical relationship between derivatives of the mixture critical properties and the ratio of amplitudes of composition and density difference at the critical point. Only the *ratio* is thereby fixed; we do not know the *value* of the amplitudes which are each proportional to $C_1(\zeta)$. If we consider the special case of exact corresponding states where $C_1^{(1)} = C_1^{(2)}$, and assume Eq. (62) is applicable so $C_1(\zeta) = C_1^{(1)} = C_1^{(2)}$, then $\Delta\rho/\rho_c(\zeta)$ is the same function of t for the pure fluids ($\zeta = 0$ or 1) as for the mixture, $0 < \zeta < 1$. However, $\Delta x \rightarrow 0$ for the pure fluid. Thus the overall measure of phase change (difference in the properties of the coexisting fluids), as a function of distance from the critical line would appear to be larger for the mixture than for the pure fluid in this example.

We first addressed this problem in Ref. 36, where we conjectured that there exists some total "amount of phase change" $A_0(t)$, a combination of Δx and $\Delta\rho$, which "obeys corresponding states" in the sense that it is nearly independent of ζ in the asymptotic limit of small $|t|$. We initially chose a quadratic combination for $A_0(t)$,

$$A_0(t) = \left\{ (\Delta\rho)^2 + 2\bar{C}_X [\rho_c(\zeta)]^2 (\Delta x)^2 \right\}^{1/2} / \rho_c(\zeta)$$

$$\approx \frac{\Delta\rho}{\rho_c(\zeta)} \left[1 + \bar{C}_X [\rho_c(\zeta)]^2 \left[\frac{\Delta x}{\Delta\rho} \right]^2 \right] \quad (73)$$

to leading order in Δx , where \bar{C}_X is an adjustable parameter set equal to 1 in Ref. 36. This quadratic combination was used by Al-Sahhaf et al. [32] to study VLE of several fluids in the critical region. However in subsequent work Rainwater and Moldover [6] replaced Eq. (73) by a linear combination, i.e.

$$A(t) = \frac{\Delta\rho}{\rho_c(\zeta)} + \left[1 + C_X |\alpha_2(\zeta)| \right] \quad (74)$$

The switch to a linear combination was motivated in part by a conjectured analogy with revised scaling [23] as discussed below Eq. (61). In revised scaling, t is altered in Eq. (45) by a small linear admixture with h , and there may be some empirical or mathematical connection with the idea of linearly mixing Δx with $\Delta \rho$. An explicit connection, however, is as yet undemonstrated and must await a future study of the mixture one-phase region.

From Eqs. (64) and (65), $A_0(t)$ is asymptotically proportional to $(-t)^\beta$. If $C_1^{(1)} = C_1^{(2)}$, the constant of proportionality for $A_0(t)$ may be made independent of ζ by the choice

$$C_1(\zeta) = \frac{C_1^{(1)}}{1 + C_X \zeta (1-\zeta) |\bar{Q}(\zeta, 0)| / \rho_c(\zeta)} \quad (75)$$

It should be emphasized that $A_0(t)$ is independent of ζ only in the asymptotic limit of small $|t|$, not over the entire VLE critical region in (ζ, t) space. For the latter condition to be satisfied, C_1 would need to be a function of t as well as ζ . However, it is explicit in the development of Sec. 2 that, whereas any function $C_i(\zeta)$ obeying the boundary conditions leads to a thermodynamically consistent model, C_i clearly cannot depend on t or h .

For $C_1^{(1)} \neq C_1^{(2)}$, the natural generalization of Eq. (75) is to replace the numerator by a linear interpolation in ζ . Furthermore, we have found that for some mixtures sufficiently far from azeotropy, the fit is substantially improved by replacing C_X with $C_X(1 + C_Y \zeta)$, where C_Y is a second adjustable parameter that, in effect, makes C_X linearly ζ -dependent. The final expression for $C_1(\zeta)$ is thus

$$C_1(\zeta) = \frac{C_1^{(2)} + \zeta [C_1^{(1)} - C_1^{(2)}]}{1 + C_X (1 + C_Y \zeta) |\alpha_2(\zeta)|} \quad (76)$$

The above equation may be straightforwardly generalized. C_X was first introduced in Ref. 6, whereas C_Y is new except for brief mention in Ref. 29. As with our subsequent parameters, setting C_X or C_Y equal to zero (equivalent to not introducing them in the first place) reduces the model to that of Moldover and Gallagher [3,4]. Our guidelines are that C_X is necessary only if $\alpha_{2m} > 0.10$ and C_Y only if $\alpha_{2m} > 0.17$.

On intuitive grounds, one would expect that C_X should always be positive, since $A_0(t)$, whatever its precise functional form, should be a monotonically increasing function of $\Delta\rho$ and Δx . However, our correlation of the carbon dioxide + hydrogen sulfide system [37] appears to require a negative C_X . This is an anomalous result; more than 30 other normal mixtures we have successfully correlated require C_X to be either positive or zero, as will be discussed in Part II of this series.

As pointed out by Griffiths and Wheeler [12], there are three independent density variables for the binary fluid mixture, which may be chosen as the density ρ , the composition x , and the entropy per mole s . It thus might be argued that $A_0(t)$ should include a contribution from Δs , the change in entropy per mole across the phase boundary, e.g.

$$A_0(t) = \frac{\Delta\rho}{\rho_c(\zeta)} \left[1 + C_X |\alpha_2| + C_S |\alpha_1| \right] = \frac{\Delta\rho}{\rho_c(\zeta)} + C_X \Delta x + R^{-1} C_S \Delta s \quad (77)$$

and thus incorporation of Δs into a new definition of $A_0(t)$ requires the evaluation of α_1 . Unfortunately, to do this we need explicitly the value of K in the definition of ζ , but in our model K is "indeterminate". Specifically, for $h = 0$, Onuki [33] shows that

$$\alpha_1 = -\rho^{-1} \left[\frac{\partial(T\omega)}{\partial T} \right]_{\Delta} = -\rho^{-1} \left[\omega + T \left[\frac{\partial\omega}{\partial\zeta} \right]_{\tau} \left[\frac{\partial\zeta}{\partial T} \right]_{\Delta} + T \left[\frac{\partial\omega}{\partial\tau} \right]_{\zeta} \left[\frac{\partial\tau}{\partial T} \right]_{\Delta} \right] \quad (78)$$

where $\Delta = \mu_2 - \mu_1$. However, even for the simple case of a constant K ,

$$\left[\frac{\partial\zeta}{\partial T} \right]_{\Delta} = \frac{\Delta}{RT^2} \zeta (1 - \zeta) = -\zeta (1 - \zeta) \ln \left[\frac{\zeta K}{1 - \zeta} \right] / T \quad (79)$$

and thus we cannot employ a revised $A_0(t)$ as redefined by Eq. (77), even though it may be fundamentally more appropriate.

Onuki calculates explicitly both α_1 and α_2 along the critical line for the helium 3 + helium 4 mixture according to the fit of Leung and Griffiths [2]. The calculation of α_1 was possible only because Leung and Griffiths explicitly evaluated K for the mixture by means of specific heat data from absolute zero to the temperature for VLE. Subsequent applications [3-4,6-8,27-29] of the Leung-Griffiths method to other mixtures have left K indeterminate.

It is, in fact, interesting and convenient that ease of experimental measurement correlates inversely with the need for knowledge about K . For correlation of usual VLE data in P , T , x and ρ , K drops out of the equations and nothing must be known about it. For the less frequently measured enthalpy, knowledge of dK/dT is necessary. Finally, for such normally unmeasured quantities as the entropy and Gibbs or Helmholtz free energies, an explicit value of K is required.

A negative value of C_X is not entirely unreasonable in that a mixture may have, in relative terms, a much larger entropy change than its constituent pure fluids. In this case, a negative C_X might be necessary to make $A_0(t)$ as redefined by Eq. (76) independent of ζ . Nevertheless, we should expect that for a substantial majority of mixtures C_X is non-negative.

It would be equivalent, and perhaps more to the taste of some, to write $C_1(\zeta)$ as a linear interpolation plus a polynomial series, e.g. a truncated sum of terms of the form $\zeta^n (1 - \zeta)$, n an integer, with adjustable coefficients. However, we find the explicit tie with α_2 intuitively appealing, and our formalism leads to a somewhat regular pattern in C_X with increasing α_{2m} . In fact, according to our experience with binary mixture VLE data, C_X is nearly linear in α_{2m} , which might lend support to a return to the quadratic coupling of Eq. (73) and Ref. 36 with a nearly universal \bar{C}_X . But while such inter-mixture comparisons support a quadratic model, intra-mixture analysis or fits of different dew-bubble curves for the same mixture tend to favor a linear model.

For $C_2(\zeta)$, the slope of the rectilinear diameter, we use the frankly empirical expression

$$C_2(\zeta) = C_2^{(2)} + \zeta C_2' + C_R x_c(\zeta) [1 - x_c(\zeta)] \quad (80)$$

where C_2' is defined by Eq. (63) and the adjustable parameter C_R , again a deviation from linear interpolation, is new here except for brief mention in Ref. 29. Here $x_c(\zeta)$ is the critical composition as a function of ζ , and, as previously stated, equals $(1-\zeta)$ for $\alpha_{2m} < 0.25$. Thus for nearly azeotropic mixtures the last term in Eq. (80) is $C_R \zeta(1-\zeta)$, but we have found for mixtures far from azeotropy that use of $x_c(\zeta)$ provides a superior fit.

Our guidelines are that C_R is necessary only if $\alpha_{2m} > 0.17$. For all mixtures studied to date, C_R , if needed, is positive and increases fairly rapidly with α_{2m} .

5. Specification of the Function $\bar{H}(\zeta, t)$

At this point we have completed the specification of the thermodynamic potential $\omega(\zeta, t, h)$, but not the model as a whole. In particular, specification of the function $\bar{H}(\zeta, t)$ is still necessary for determination of the coexisting compositions.

From Eq. (33), we see that on the critical locus

$$x_c(\zeta) - 1 - \zeta + \zeta(1 - \zeta) \bar{H}(\zeta, t = 0) \quad (81)$$

As previously stated, for mixtures not too far from azeotropy we make the restriction that $x_c(\zeta) = 1 - \zeta$, which implies the condition $\bar{H}(\zeta, t = 0) = 0$. Furthermore, as there is no reason to suppose that \bar{H} is nonanalytic, we can expand \bar{H} as a power series in t with ζ -dependent coefficients. For the range of applicability of the model, it turns out that a linear term in t is sufficient.

However, as was also noted in the previous section, for $\alpha_{2m} > 0.25$ we cannot simultaneously set $x_c = 1 - \zeta$ and assume linear interpolation for $C_i(\zeta)$ in Eq. (61). The objectives of this section are therefore twofold, first to extend the model to mixtures far from azeotropy with a nonzero \bar{H} at $t = 0$, and second to model the contribution to \bar{H} which is linear in t and is present for almost all mixtures.

As motivation for our strategy, we first prove that in the dilute limits (small x or small $x_1 = 1 - x$), the distance from azeotropy α_2 , which largely governs the shape of the coexistence surface, is to leading order independent of $dx_c/d\zeta$. Consider Eq. (69) for a dilute solution of fluid 2 in fluid 1, i.e.

$$\alpha_2 = (R\rho_c)^{-1} \zeta(1 - \zeta) \frac{dx}{d\zeta} \left\{ \frac{d}{dx} \left[\frac{P_c}{T_c} \right] + \left[\frac{d}{dx} \left[\frac{1}{T_c} \right] \right] \left[T_c \left[\frac{dP}{dT} \right]_{1c}^{\sigma} - P_c + O(x) \right] \right\} \quad (82)$$

where $(dP/dT)_{1c}^{\sigma}$ is the slope of the vapor pressure curve of fluid 1 at its critical point. Because of the boundary conditions on the chemical potential, Eqs. (8)–(9), in the dilute limit loci of constant ζ must be parallel to the pure vapor pressure curves.

Now consider an arbitrary variation of x_c with ζ subject to boundary conditions, i.e.

$$1 - \zeta = \epsilon x + O(x^2) \quad (83)$$

where ϵ does not necessarily equal one. Expanded in a Taylor series in x , Eq. (82) becomes

$$\begin{aligned}\alpha_2 &= (R\rho_{c1})^{-1} \epsilon x (-1/\epsilon) \left\{ \frac{d}{dx} \left[\frac{P_c}{T_c} \right]_{x=0} \right. \\ &\quad \left. + \left[\frac{d}{dx} \left[\frac{1}{T_c} \right] \right]_{x=0} \left[T_c \left[\frac{dP}{dT} \right]_{1c}^{\sigma} - P_c \right] \right\} + O(x^2) \\ &= -(R\rho_{c1} T_{c1})^{-1} x \left\{ \left[\frac{dP_c}{dx} \right]_{x=0} - \left[\frac{dP}{dT} \right]_{1c}^{\sigma} \left[\frac{dT_c}{dx} \right]_{x=0} \right\} + O(x^2)\end{aligned}\tag{84}$$

Thus to leading order α_2 is independent of ϵ and depends on quantities that are experimentally measurable. The ratio of the amplitudes of Δx and $\Delta \rho$ is then fixed by the critical properties and vapor pressure curve of the solvent and the initial slope of the critical line. Since $C_1(\zeta)$ is presumably analytic in ζ and therefore x , the leading-order amplitudes of Δx and $\Delta \rho$ separately are also determined by these measurable quantities. Similar arguments apply to a dilute solution of fluid 1 in fluid 2.

The importance of the combination of derivatives in brackets in Eq. (84) was first noted by Krichevskii [38] and later by Rosen [39], who defined a quantity A as

$$A = \left[\frac{dP_c}{dx} \right]_{x=0} - \left[\frac{\partial P}{\partial T} \right]_{1c}^{\sigma} \left[\frac{dT_c}{dx} \right]_{x=0}\tag{85}$$

so that $\alpha_2 = -(R\rho_{c1} T_{c1})^{-1} Ax + O(x^2)$.

Levelt Sengers and co-workers [34,40–42] have shown that a wide range of thermodynamic properties, particularly excess molar volumes, are dependent on A for dilute mixtures. While many of these properties involve thermodynamic paths off the coexistence surface ($h = 0$), or derivatives in directions away from the coexistence surface, Levelt Sengers [35] has shown that on the VLE surface the slope dP/dx of the so-called "bird's beak" isotherm $T = T_{c2}$ (the critical temperature of the more volatile component) is equal to A .

Rizvi et al. [43] have suggested that a theory of dilute solutions based on A may be useful in understanding supercritical solubility, and may be a preferred alternative to our methods which normally require extensive and high-quality VLE data. Supercritical solubility is quantitatively described by the behavior of the dew curves of a mixture with a large α_{2m} , e.g. carbon dioxide + toluene, near the critical point of the more volatile component. Unfortunately, as shown by the 0.96 propane + 0.04 n-octane mixture in Part II of this series, the formal expressions for the dilute model break down much more rapidly for this case than for mixtures rich in the less volatile component or for mixtures with smaller α_{2m} .

As explained in Sec. 2, the degrees of freedom embodied in $K(T)$ allow the construction of many different but equivalent modified Leung-Griffiths models, with different functions $x_c(\zeta)$ but the same P - T - x - ρ VLE surface. If $T_c(x)$ is monotonic, a choice of $K(T)$ has been proven to exist such that $x_c = 1 - \zeta$. We expect that another choice of $K(T)$ exists such that, at least in some best-fit sense, loci of constant ζ are parallel to the pure vapor pressure curves, or more precisely Eqs. (62)–(63) hold for $3 \leq i \leq 6$. The empirical principle of Sec. 4 states that, for small α_{2m} , these choices of $K(T)$ are essentially identical.

Since the empirical principle does not lead to accurate VLE fits for $\alpha_{2m} > 0.25$, we must assume that the above two choices of $K(T)$ begin to diverge at this point. We then have our choice whether to retain the condition $x_c = 1 - \zeta$ or to retain the condition of parallel constant- ζ curves.

We elect to retain the latter condition, for two reasons. First, it allows us to retain a physically appealing, nonadjustable relationship between a (P, T) data point and a point on the critical locus. Equations (29) and (61) define a mapping from (ζ, t) to (P, T) and vice versa, which is one-to-one for normal mixtures and two-to-one in some regions for azeotropic mixtures. If the parallel structure of constant- ζ lines is unaltered, a given (P, T) point is always associated with the same point on the critical locus as a function of x (if not ζ), and t for that datum is unaltered.

Second, we can exploit the observation that the model is insensitive to $dx_c/d\zeta$ at the dilute limits. For maximum adjustability, as seen from Eq. (69), we need the ability to vary $dx_c/d\zeta$ for the equimolar mixture. Our choice for $x_c(\zeta)$ to achieve such adjustability is

$$x_c(\zeta) = 1 - \zeta + H_1 \zeta (1 - \zeta)(1 - 2\zeta) \quad (86)$$

$$\frac{dx_c}{d\zeta} = -1 + H_1 (1 - 6\zeta + 6\zeta^2) \quad (87)$$

and, from Eq. (80)

$$\bar{H}(\zeta, t = 0) = H_1 (1 - 2\zeta) \quad (88)$$

The second term in Eq. (87) has an extremum at $x = 1/2$, so variation of H_1 has the greatest effect on the equimolar mixture, as desired.

We have introduced for the first time (except for brief mention in Ref. 29) a fourth adjustable parameter H_1 , with guidelines that it be used only if $\alpha_{2m} > 0.25$. There are obvious outer bounds for this parameter; $H_1 < 1$ ensures that $0 < x_c < 1$ and $H_1 > -2$ ensures that $dx_c/d\zeta$ is always negative. The bounds to ensure thermodynamic stability over the entire surface are not established but are probably much more restrictive. In practice, we have kept $|H_1| \leq 0.65$ for all correlations to date.

Before considering the t -dependence of \bar{H} , it is appropriate to establish a range of applicability for the present model. Since it is specifically designed for critical conditions, it should be expected to work only within a certain distance from the critical line. The variable which measures such a distance is $(-t)$, and since the thermodynamic potential is expressed as a nonanalytic power series in this expansion parameter, the model should be quantitatively correct only when the expansion parameter is an order of magnitude less than unity, say $-0.1 < t < 0$. Moreover, for pure fluids, and consequently for our mixture model, for $t < -0.1$ Eq. (60) on the vapor side enters the regime when the virial equation of state is applicable, and begins to deviate significantly from that virial equation.

However, along a pure vapor pressure curve or a line of constant ζ

$$\lim_{T \rightarrow T_c(\zeta)} \left[\frac{\partial \ln P}{\partial \ln T} \right]_{\zeta} = 1 + C_4(\zeta) \quad (89)$$

and, typically, $C_4 \approx 6$. Because of the steepness of the vapor pressure curve near critical, a ten percent decrease in temperature corresponds approximately to a 50 percent decrease in pressure. On a P - T graph, therefore, the "extended critical region" for VLE is bounded by the critical line, the two pure vapor pressure curves, and the locus $t = -0.1$ which is approximately the locus $P = P_c(\zeta)/2$, as shown in Fig. 5. It is within this region that conventional, analytic equations of state typically break down, so, as emphasized in App. A, our model and analytic equations of state complement each other.

Within this extended critical region, we find that only a linear dependence of \bar{H} on t is needed, in contrast to ω_{an} of Eq. (42) for which the truncation is at the cubic term. We again follow the approach taken by Moldover and Gallagher [4] in their Appendix B. As a function of ζ and τ , according to Eq. (34), \bar{H} when expanded in a power series in τ becomes

$$\bar{H}(\zeta, \tau) = \bar{H}(\zeta, 0) + \tau \left[\left[\frac{\partial^2 H}{\partial \zeta \partial \tau} \right]_{\tau=0} + \frac{dB_c(\zeta)}{d\zeta} \left[\frac{\partial^2 H}{\partial \tau^2} \right]_{\tau=0} \right] + O(\tau^2) \quad (90)$$

In the limit of pure fluid 2 ($\zeta \rightarrow 0$), from Eqs. (9) and (12)

$$H(0, \tau) = \nu_2^\sigma + \ln K_2 = \frac{\mu_2^\sigma}{RT} + \ln K_2 \quad (91)$$

where the superscript σ again denotes the value on the saturation curve. The first term in the brackets of Eq. (90) is difficult to interpret physically, but the partial derivative in the second term for pure fluid 2, with Eq. (11), may be written

$$\left[\frac{\partial^2 H}{\partial \tau^2} \right]_{\zeta=\tau=0} = RT^3 \frac{d^2 \mu_2^\sigma}{dT^2} \quad (92)$$

where the possible T -dependence of K_2 has been neglected. In terms of t instead of τ , to linear order the contribution to \bar{H} is

$$\frac{dB_c(\zeta)}{d\zeta} \left[\frac{\partial^2 H}{\partial \tau^2} \right]_{\tau=0} \tau = - \frac{1}{T_c(\zeta)} \frac{dT_c(\zeta)}{d\zeta} C_H t \quad (93)$$

where

$$C_H = \lim_{T \rightarrow T_c} \frac{T}{R} \frac{d^2 \mu_2^\sigma}{dT^2} \quad (94)$$

Moldover and Gallagher [4] estimate, from consideration of consequences of the van der Waals equation and fits to some pure fluid data, that $C_H \approx -12$ for pure propane. In their model for VLE of propane + n-octane they chose $C_H = -25$, although a reexamination of that mixture, as will be shown in Part II of this series, suggests that $C_H \approx -15$ at the pure propane end.

In our model, we treat C_H as an adjustable parameter, neglect the first term in brackets of Eq. (90), and in effect assume that Eq. (93) is applicable for all ζ , not just $\zeta = 0$ or $\zeta = 1$. In fact, it has been found that minus twelve is a typical value for C_H . For mixtures, sufficiently far from azeotropy, it has also been found that the fit can be improved by allowing a linear dependence of C_H on ζ , i.e. $C_H \rightarrow C_H(1 + C_Z\zeta)$ where C_Z is also an adjustable parameter. This is analogous to the replacement of C_X by $C_X(1 + C_Y\zeta)$ in Eqs. (75)–(76). In summary, our model for H is

$$\bar{H}(\zeta, t) = H_1(1 - 2\zeta) - \frac{1}{T_c(\zeta)} \frac{dT_c(\zeta)}{d\zeta} C_H(1 + C_Z\zeta) t \quad (95)$$

where C_H and C_Z have appeared in several previous papers [6,8,29].

Our guidelines are that C_H may be used for all mixtures, whereas C_Z is used only if $\alpha_{2m} > 0.17$. The only mixture for which we have set $C_H = 0$ is helium 3 + helium 4, the subject of the original Leung–Griffiths work [2].

As with $C_1(\zeta)$, it would be essentially equivalent, and perhaps more to the taste of some, to replace the second term of Eq. (95) by (t) times a simple polynomial in ζ with adjustable coefficients, rather than by tying this term to $dT_c/d\zeta$. However, we have found the above form to be convenient in that C_H lies in a fairly restricted interval (usually $-15 \leq C_H \leq -6$) over a range of mixtures for which $dT_c/d\zeta$ can differ by an order of magnitude or more.

The modeling of $\bar{H}(\zeta, t)$ rather than $H(\zeta, t)$ is convenient for the calculation of the P–T–x– ρ coexistence surface (or one-phase region), but is done at some expense to the calculation of other thermophysical properties. For example, it would be of interest to correlate the chemical potentials μ_1 and μ_2 as functions of P and T. If $H(\zeta, t)$ were modeled, as well as $\omega(\zeta, t)$, then the equations for H and the definition of ζ , Eq. (7), provide two algebraic equations for two "unknowns", μ_1 and μ_2 , in terms of "known" quantities ζ and t . These can be solved for the chemical potentials, after which the Gibbs free energy can be calculated from Eq. (2) and other properties such as entropy from

the usual thermodynamic relations; see Eqs. (2.37) – (2.40) of Leung and Griffiths [2]. We see that, as with the entropy difference of Eqs. (77) – (78), calculation of the total entropy requires explicit knowledge of K .

In the present formalism where $\bar{H}(\zeta, t)$ is modeled instead, the "unknown" μ_1 and μ_2 are represented by one algebraic equation and one partial differential equation, Eq. (34), so their calculation would be much more difficult. Also the enthalpy, as calculated from Eqs. (6) and (28), requires $(\partial H / \partial \tau)_{\zeta}$ by itself, as well as in combination with $(\partial H / \partial \zeta)_{\tau}$ according to Eq. (34). Consequently, in future correlations of the enthalpy it probably will be necessary, after correlating the P – T – x – ρ surface and obtaining a model $\bar{H}(\zeta, t)$, to solve Eq. (34) as a partial differential equation, subject to the boundary condition of Eq. (91), and thereby obtain a self-consistent $H(\zeta, t)$. In summary, the simplicity of calculating the P – T – x – ρ surface comes at the price of complexity for other thermodynamic functions.

6. Representation of the Critical Locus

As a final item, we require representations of the mixture critical pressures, temperatures, and densities as functions of ζ or, equivalently, as functions of x . Typically the experimentalist provides a table of these critical properties for the composition that were measured. We first fit the equations below to the experimentalist's table, but the coefficients are understood to have a limited adjustability, in the sense that a slightly different critical locus from that reported by the experimentalist may, within our model, provide a better fit to the coexistence surface. As functions of x , the representations we choose are

$$\begin{aligned} \frac{1}{RT_c(x)} = & \frac{1-x}{RT_{c1}} + \frac{x}{RT_{c2}} + x(1-x) \left[T_1 + (1-2x) T_2 \right. \\ & \left. + (1-2x)^2 T_3 + (1-2x)^3 T_4 \right] \end{aligned} \quad (96)$$

$$\begin{aligned} \frac{P_c(x)}{RT_c(x)} = & \frac{(1-x)P_{c1}}{RT_{c1}} + \frac{xP_{c2}}{RT_{c2}} \\ & + x(1-x) [P_1 + (1-2x) P_2 + (1-2x)^2 P_3 + (1-2x)^3 P_4] \end{aligned} \quad (97)$$

$$\rho_c(x) = (1-x) \rho_{c1} + x \rho_{c2} + x(1-x) [\rho_1 + (1-2x) \rho_2 + (1-2x)^2 \rho_3] \quad (98)$$

where P_{ci} , T_{ci} and ρ_{ci} are the critical parameters for pure fluid i . Since experimental sources typically provide dew–bubble curves for five or six mixtures, from the critical point tables alone the introduction of more than three or four degrees of freedom in Eqs. (85)–(87) would lead to overfitting. For most mixtures, only the terms through T_3 and P_3 are actually used.

Rainwater and Moldover [6] have developed an alternative to Eqs. (97)–(98) which we employ in the present model for nonazeotropic mixtures. They introduced a new variable x_T ,

$$x_T = \frac{1/T_{c1} - 1/T_c(x)}{1/T_{c1} - 1/T_{c2}} \quad (99)$$

which has the property that $x_T = 0$ when $x = 0$ and $x_T = 1$ when $x = 1$, and for the mixture is only a function of $T_c(x)$. If $T_c(x)$ is monotonic in x , x_T varies smoothly from 0 to 1 as x varies over the same interval. In the alternative formulation, the polynomials in x of Eqs. (96)–(97) are replaced by polynomials in x_T , i.e.

$$\frac{P_c(x)}{RT_c(x)} = \frac{(1-x_T)P_{c1}}{RT_{c1}} + \frac{x_T P_{c2}}{RT_{c2}}$$

$$+ x_T(1-x_T) \left[\bar{P}_1 + (1-2x_T) \bar{P}_2 + (1-2x_T)^2 \bar{P}_3 + (1-2x_T)^3 \bar{P}_4 \right] \quad (100)$$

$$\rho_c(x) = (1-x_T) \rho_{c1} + x_T \rho_{c2} + x_T(1-x_T) \left[\bar{\rho}_1 + (1-2x_T) \bar{\rho}_2 + (1-2x_T)^2 \bar{\rho}_3 \right] \quad (101)$$

Equations (100)–(101) have a practical advantage for fitting over Eqs. (97)–(98), in that the former determine the critical line in pressure versus temperature or temperature versus density respectively. Thus adjustments made in Eq. (96), with the parameters of Eqs. (100)–(101) held constant, will not affect the shape of the critical line on a P – T graph or a T – ρ graph. This would not be the case if Eqs. (97)–(98) were used instead. However, for most azeotropic mixtures $T_c(x)$ has a minimum, and since x_T no longer is single-valued, a correlation therefore must be made in x .

In principle, the fitting of the critical line is a separate problem from use of the modified Leung–Griffiths or any other thermodynamic model, and the number of parameters needed for a quality fit depends on the length and curvature of the critical line for the mixture under consideration. Usually, only three degrees of freedom in Eqs. (96) and (100) or (97) are needed, but there are counterexamples. For carbon dioxide with n-butane [29] or a heavier alkane, the P–T critical locus is nearly linear near the alkane end and curves abruptly near carbon dioxide. We have found that a fourth degree of freedom in Eqs. (96) and (100) is absolutely essential to reproduce the critical locus and dew–bubble isotherm in the high temperature range.

The specification of the thermodynamic model is now complete. The coexistence surface in P–T– ρ –x space is given by Eq. (60) and Eq. (33), where the explicit representation of the function $Q(\zeta, t)$, from Eqs. (32), (41), (42), (45), (47) and (63), with $\theta^2 = 1$, $\alpha = 0.1$ and where $dx/d\zeta$ is given by Eq. (87) on the critical locus, is

$$\begin{aligned} \bar{Q}(\zeta, t) = & \frac{dx}{d\zeta} \frac{PT_c(x)}{RT P_c(x)} \frac{d}{dx} [P_c(x)/T_c(x)] \\ & + \frac{P_c(x)}{RT_c(x)} \left[C'_3 (-t)^{1.9} + C'_4 t + C'_5 t^2 + C'_6 t^3 \right] \\ & + \frac{dx}{d\zeta} \frac{P_c(x)}{R} \frac{d[1/T_c(x)]}{dx} (1+t) \left[-1.9 C_3(\zeta) (-t)^{0.9} + C_4(\zeta) \right. \\ & \left. + 2 C_5(\zeta) t + 3 C_6(\zeta) t^2 \right]. \end{aligned} \quad (102)$$

For many mixtures, $H_1 = 0$ so $dx/d\zeta = -1$.

Excluding the pure fluid critical points, the model can have as many as 29 parameters. However, all but six are fixed by the pure–fluid coexistence properties and the critical line. The first set of parameters, which characterizes the pure fluid vapor pressure and temperature–density coexistence curves, is $C_j^{(i)}$, $i = 1, 2$ and $j = 1, \dots, 6$ of Eqs. (37) and (39) (although frequently $C_6^{(i)}$ is not used). The second set of parameters, which characterizes the critical line, is T_i and P_i or \bar{P}_i , $i = 1, 2, 3, 4$ and ρ_i or $\bar{\rho}_i$, $i = 1, 2, 3$ of Eqs. (96)–(101). Finally, the parameters C_x and C_y of Eq. (76), C_R of Eq. (80), H_1 of Eq. (88) and C_H and C_Z of Eq. (95) are properties of the entire coexistence surface of the mixture.

Our model has been and continues to be under development. As α_{2m} increases, more parameters will be necessary, and we will develop guidelines as to what parameters are necessary and permissible for a given value of α_{2m} . A previous edition of the model [6,7], with only C_H , C_X and C_Z , was found to be satisfactory for the P-T-x surface if $\alpha_{2m} < 0.25$ and for coexisting densities if $\alpha_{2m} < 0.17$. The present edition extends the range of P-T-x correlation to (at least) $\alpha_{2m} = 0.3$ and the range of density correlation to $\alpha_{2m} = 0.25$. With our guidelines, we believe the model can fit quality VLE data to within their precision while not overfitting, and can be used as a data evaluation technique to identify erroneous data.

While a systematic study has yet to be undertaken, it appears that α_{2m} has an upper bound of about 0.7 to 0.8 for Type I binary mixtures. If the pure fluids are too dissimilar the critical locus "breaks" and becomes discontinuous. For example, methane ($T_c = 190.55$ K) forms a continuous critical locus with 2,2 dimethylbutane, the hexane isomer with the lowest critical temperature ($T_c = 488.7$ K), but a discontinuous critical locus with the four other hexane isomers [44]. We are working towards the addition of new features onto the model to extend its range, and the present sub-project will be considered complete when the model incorporates sufficient features to yield an accurate P-T-x- ρ coexistence surface up to $\alpha_{2m} \approx 0.8$.

7. Summary

This report has provided a detailed and self-contained presentation of a thermodynamic model to describe VLE of Class I binary mixtures over an extended critical region. The model is based on that of Leung and Griffiths [2] as modified by Moldover and Gallagher [3,4], but with considerable subsequent development. Insights are presented based on our experience and hindsight from successfully correlating 35 binary mixtures to date. Conjectures of possible ways to improve and to extend the range of the model are included.

We have attempted here to examine carefully the logical structure of the model. The formalism is in part rigorous thermodynamics, in part incorporation of a simplified modern understanding of critical phenomena, and in part empiricism, although motivated as far as possible by heuristic principles such as corresponding states as well as rigorous boundary conditions.

The new results and insights of this report, not included in previous publications, are as follows:

- A. The "constant" K (or K_1 or K_2) in the definition of ζ , Eq. (7), is generalized to a temperature-dependent function. In particular, it has been shown that the formal expressions for the P - T - x - ρ surface are left unchanged.
- B. With a generalized K , new terms proportional to dK/dT are derived for the energy density u , Eq. (28), and consequently the (measurable) coexisting enthalpy.
- C. It is demonstrated that the temperature dependence of K includes and extends the degrees of freedom available from the choice of zeroes of chemical potential. Also, it is explicitly shown that chemical potential shifts of μ_{10} and μ_{20} lead to a shift in energy density of $\rho_1 \mu_{10} + \rho_2 \mu_{20}$, as required.
- D. From Eq. (36), it is demonstrated that for monotonic $T_c(x)$ a $K(T)$ exists such that $x_c(\zeta) = 1 - \zeta$, or within limits x_c equals any other function such that $x_c = 1$ for $\zeta = 0$ and vice versa, exactly.
- E. A relationship is derived, Eq. (71), between α_2 , the reduced ratio of composition and density amplitudes, and the slope of isopleths on a T - ρ diagram at critical.
- F. An empirical principle is affirmed that, for $\alpha_{2m} = \max |\alpha_2|$ sufficiently small, the model with $x_c = 1 - \zeta$ on critical coincides with the model with loci of constant ζ linearly interpolated between the pure vapor pressure curves, according to Eqs. (62)–(63).
- G. A new parameter C_Y is introduced in Eq. (76). It was briefly mentioned (as were C_R and H_1) in Ref. 29.
- H. It is shown that calculation of Onuki's [33] α_1 , the reduced ratio of entropy and density amplitudes, requires explicit knowledge of K , unavailable from usual VLE correlations with the model.
- I. A new parameter C_R , that adjusts the slope of the rectilinear diameter, is introduced in Eq. (80).

- J. It is proven that, in the leading-order dilute limit, α_2 is independent of $dx_c/d\zeta$, and depends only on quantities which are experimentally measurable, the slopes of the solvent vapor pressure curves and the critical locus.
- K. With motivation from the previous result, a new parameter H_1 is introduced in Eq. (95).

Furthermore, the modified Leung-Griffiths model is compared and contrasted with conventional phase equilibrium calculation techniques in App. A and with the "original" Leung-Griffiths model [2,28,29] in App. C. Nevertheless, the primary justification for this work is its success in correlating VLE for a wide variety of binary mixtures, as is demonstrated in Part II of this series.

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Appendix A

Comparison with Conventional Equations of State

In this appendix we give a brief overview of conventional VLE calculation techniques and their difficulties in the critical region, and contrast them with the present model. Phase equilibrium is of course extremely important to the chemical and petroleum industries, and many different equations of state and computer packages have been developed [45]. For low pressures, in particular atmospheric pressure, these equations and packages largely fulfill industrial needs.

However, such conventional methods *in principle* have deficiencies at critical pressures. Our model, being essentially an expansion about critical conditions with correct critical exponents, usually yields accurate VLE calculations from the critical pressure down to about half that pressure, below which conventional methods are generally reliable. Thus our model is intended to supplement, not to supersede, classical methods.

By conventional definition, an equation of state for a binary mixture takes the form

$$P = P(T, \rho, x) \quad (A1)$$

and is therefore a mixed representation of a field variable (pressure) as a function of one field variable (temperature) and two density variables (density and composition). The analogous expression in our model is $\omega(\zeta, \tau, h)$, Eqs. (41), (42) and (45)–(47), which involves only field variables.

While modern liquid–state theories have made progress in predicting an equation of state microscopically [1], in practice empirical forms are usually employed. Of course, it is considerably easier to correlate the VLE surface alone than to correlate the entire thermodynamic volume (liquid and gas), so simple cubic equations or variants of the van der Waals equation, e.g. Redlich–Kwong [46], Peng–Robinson[47], etc., are frequently utilized for VLE correlations. For a more global thermodynamic description, many–parameter equations of state such as the Benedict–Webb–Rubin (BWR) equation [48] are typically used.

Equations of state are usually developed first for pure fluids. To generalize them to mixtures, the parameters of the equation are made composition–dependent by means of various mixing and combining rules. Our expressions for $C_i(\zeta)$ in Sec. 4 can be viewed as the analog of mixing rules. An important difference is that in conventional methods a liquid state of composition x_ℓ is matched with a coexisting vapor state of a different

composition x_v , and thus the equation-of-state parameters across the phase boundary are different for liquid and vapor. However, our "mixing rules" use ζ rather than x , and ζ is the same for liquid and vapor. The latter picture may be the more natural.

The specific equations of state cited above have the property that the chemical potentials μ_1 and μ_2 may be calculated by analytical integration. The VLE surface is mapped out by various algorithms, e.g. "flash calculations," which search numerically for liquid and vapor state points at the same pressure and temperature such that chemical potentials, or equivalently fugacities, are equal. The most commonly used algorithm is described in detail by Ely [49].

There are two problems associated with conventional VLE calculations in the extended critical region, in our formalism $-0.1 < t < 0$ and particularly for very small $|t|$. The first problem is that many algorithms converge slowly or not at all near the critical locus. Knapp et al. [50] present a large number of P-x diagrams with isothermal VLE data and calculated dew-bubble curves similar to Fig. 3. The calculated curves, in most cases based on the Peng-Robinson equation [47], frequently end at pressures below critical and in some cases are not presented at all for the highest isotherms.

However, any reasonably well-behaved equation of state does contain within it a prediction of the critical line, which is the locus of points satisfying the condition

$$\left[\frac{\partial^2 G_m}{\partial x^2} \right]_{P,T} = \left[\frac{\partial^3 G_m}{\partial x^3} \right]_{P,T} = 0 . \quad (A2)$$

where G_m is the Gibbs free energy per mole. Furthermore, the equation of state also contains a coexistence surface that extends up to the critical line. Thus, the failure of a particular algorithm to converge near the critical line indicates a deficiency in the calculational algorithm, not in the equation of state.

A second and fundamentally distinct problem is that conventional equations of state tend to predict an incorrect critical locus and coexistence surface near critical. The compilation of Knapp et al. [50] shows several dew-bubble curves for which the calculations begin to diverge significantly from experiment at high pressure before the limit of convergence is reached. This problem is generally more severe for wide dew-bubble curves or, in our terminology, large $|\alpha_2|$. Streett and co-workers [51-53] have demonstrated for mixtures with relatively small $|\alpha_2|$ that the data and predictions of cubic equations diverge near critical.

In our view, this second problem is a manifestation of a fundamental shortcoming of classical equations of state. If, in Eq. (A1), P is an analytic function of T , ρ , and x , the critical exponents *must* in the asymptotic limit reach certain classical (and incorrect) values; α , of Eq. (38), classically is zero compared to the established "nonclassical" value of 0.110; β of Eq. (39), classically is one-half rather than 0.325; γ , of Eq. (49) classically is unity rather than 1.24. The "effective" values $\alpha = 0.1$ and $\beta = 0.355$ used in our model do not coincide exactly with the true asymptotic values, but are much closer to them than the classical critical exponents.

For practical purposes, the classical value $\beta = 1/2$ in our view is a much more important cause of the failure of equations of state in the critical region, at least for VLE, than the discrepancies in other exponents. This problem is, of course, present for pure fluids as well. A classical equation of state cannot truly mathematically represent the temperature-density coexistence curve of a pure fluid, but can *mimic* it to any desired accuracy given enough terms. Schmidt and Wagner [54] have introduced a many-parameter equation of state that describes the near-critical thermodynamics of pure fluids, e.g. methane [55], quite accurately. Its generalization to mixtures requires a choice of mixing rules, etc., and is not straightforward. To our knowledge, no classical equation has yielded critical region mixture VLE correlations of the accuracy shown in Part II of this series and our previously published correlations [6-8,29].

It has been suggested that our fit quality is largely due to use of the experimental critical locus, not to the value of β that we use, and that if the parameters of a classical equation were varied to obtain the best fit to the critical locus, the VLE predictions would be comparable. We do not agree, but a resolution of this question must await an algorithm for classical equations that converges very near critical. The fit of Moldover and Rainwater [29] to the carbon dioxide + n-butane dew-bubble isotherms of Hsu, Nagarajan and Robinson [56] shows an agreement of shape with their data near critical which, as the experimentalists themselves point out, is characterized by $\beta \approx 1/3$.

In fact, the insights of the present work may be useful in developing an algorithm for VLE from classical equations that converges near critical. First, the critical line could be determined from Eq. (A2) from techniques such as those of Eaton, et al. [57] Then, our results such as Eq. (72) could be used to construct approximate asymptotic forms for dew-bubble curves near critical as functions of derivatives of the critical locus. These forms would not be exact, but as with any numerical root-finding algorithm, a good first guess should lead to rapid convergence. Here we would not be injecting the Leung-Griffiths approach into classical equations, but rather would be more efficiently calculating the

critical locus and near-critical VLE surface contained within the classical equation, using insights from Leung-Griffiths theory. With such an algorithm, a true and fair quantitative test of the relative merits of the two approaches could be conducted.

Various hybrid techniques, in part incorporating conventional approaches and in part incorporating more modern concepts of field variables and nonclassical critical exponents, have been proposed. One idea is to start with a scaling-law equation of state for a reference pure fluid, and then to construct a mixture equation of state using classical corresponding states [58]. Unfortunately, this approach does not work [59]. Contrary to experiment, the P-T critical locus in the dilute limits is co-linear with the pure vapor pressure curves [39,60]. Furthermore, the correct critical thermodynamic behavior of the mixtures is not predicted [59,61].

Fox [62] has proposed a method in which an equation of state is rewritten in terms of field variables, and a "reference" mixture is formed from two identical fluids, thus being in reality a pure fluid with arbitrarily different labels "one" and "two" for the molecules. A transformation is then made to a "target" mixture by changing a background function, or analytic part of a thermodynamic potential, of one label only, thus yielding a critical locus and coexistence surface. In Fox's initial paper [62], the resulting critical line had $P_c(x)$ variable but $T_c(x)$ a constant, though in subsequent work [63] both P_c and T_c can be varied with a reasonable amount of freedom. Whether this approach will lead to accurate P-T-x- ρ correlations of VLE for a wide variety of mixtures remains to be seen.

Admittedly, classical equations of state still do retain certain advantages over the modified Leung-Griffiths model in its present stage of development. The difficulties described at the end of Sec. 5 for calculating quantities other than P, T, ρ and x, such as enthalpy or entropy, are not present to the same degree within classical approaches. Also, at least qualitatively as van Konynenberg and Scott [9] have shown, even the van der Waals equation can predict five of the six known types of binary mixture phase equilibria. The present modified Leung-Griffiths model is restricted to Type 1 mixtures, although a generalization to Type 2 is in progress.

Additionally, of course, conventional equations of state yield superior results at temperatures and pressures well below critical, in our formalism $t < -0.1$. We believe the ultimate solution to an accurate global description of VLE will be to merge the two approaches. Hopefully, for most simple mixtures there will be an interval in t, say $-0.1 < t < -0.07$, where both approaches work. In this case, a global model could transfer

from one to the other with a switching function, or an alternative method along the lines proposed by Fox [64]. Such a merging of the modified Leung—Griffiths model with classical equations of state is planned, but is deferred until a comprehensive study of binary mixture VLE near critical has been completed.

Appendix B

Critical Divergence of the Specific Heat at Constant Volume

The objective of this appendix is to derive the relationship between the term proportional to $(-t)^{2-\alpha}$ in the pure fluid vapor pressure curve, Eq. (37) and the critical divergence of the specific heat according to Eq. (38). This is basically a small facet of the thermodynamics as predicted by scaling—law equations, which is presented in much more detail elsewhere, e.g. by Levelt Sengers et al. [26] Here we extract only the pieces from that lengthy formalism that are needed for assigning a value to C_3 .

The internal energy per unit volume is given by Eq. (28). Since H is analytic in the present formalism and there is certainly no need to use nonanalytic forms for K_1 or K_2 , the singular part of Eq. (28) is

$$u_{\text{sing}} = \left[\frac{\partial \omega_{\text{sing}}}{\partial \tau} \right]_{\zeta, h} = \left[\frac{\partial \omega_{\text{sing}}}{\partial t} \right]_{\zeta, h} \frac{t+t^2}{\tau} \quad (\text{B1})$$

where ω_{sing} is given by Eq. (47) parametrically in terms of r and θ .

The specific heat per unit volume C_v for pure fluid 2 is

$$C_v = \left[\frac{\partial u}{\partial T} \right]_{\rho, \zeta=0} = \frac{1}{T_c} \left[\frac{\partial u}{\partial t} \right]_{\rho, \zeta=0} \quad (\text{B2})$$

and similarly for pure fluid 1 where $\zeta = 1$. (We shall confine our discussion to pure fluid 2, and henceforth in this appendix it is understood that $\zeta = 0$.) From Eqs. (45)–(47), (B1) and the relation

$$\left[\frac{\partial \omega_{\text{sing}}}{\partial t} \right]_h = \frac{\partial(\omega_{\text{sing}, h}) / \partial(r, \theta)}{\partial(t, h) / \partial(r, \theta)} \quad (\text{B3})$$

we find that

$$u_{\text{sing}} = R T_c (1+t)^2 \frac{P_c C_3}{R T_c a_T} r^{1-\alpha} \frac{\sum_{n=0}^3 P_{1n} \theta^{2n}}{\sum_{m=0}^2 P_{2m} \theta^{2m}} \quad (\text{B4})$$

where P_{1n} and P_{2m} are constant coefficients. (The only coefficients that survive in the final result are $P_{10} = (2-\alpha) a_0$ and $P_{20} = (b^2 - 1)^{-1}$).

To obtain the leading-order singularity in the specific heat we replace the factor $(1 + t)^2$ by unity in Eq. (B4). We thus define

$$C_v^{\text{sing}} = \frac{1}{T_c} \left[\frac{\partial \bar{U}_{\text{sing}}}{\partial t} \right]_{\rho} \quad (\text{B5})$$

where $\bar{U}_{\text{sing}} = U_{\text{sing}} (1 + t^2)^{-1}$. Once again the partial derivative must be evaluated parametrically, i.e.

$$C_v^{\text{sing}} = \frac{1}{T_c} \frac{\partial(\bar{U}_{\text{sing}}, \rho) / \partial(r, \theta)}{\partial(t, \rho) / \partial(r, \theta)} \quad (\text{B6})$$

According to Eqs. (14), (41), (42), (45)–(47) and (59),

$$\rho(r, \theta) = \rho_c \left[1 + r C_2 \frac{1 - b^2 \theta^2}{b^2 - 1} - \theta r^\beta \frac{\sum_{n=0}^2 P_{3n} \theta^{2n}}{\sum_{m=0}^2 P_{2m} \theta^{2m}} \right] \quad (\text{B7})$$

where P_{3n} are additional constant coefficients.

Evaluation of Eq. (B6) yields C_v^{sing} as a function of r and θ . However, we are specifically interested in the behavior of C_v^{sing} along the critical isochore in the one-phase region as a function of t , since experiments along the critical isochore produce a divergence in the specific heat according to Eq. (38) and a measure of the amplitude of divergence. From Eq. (B7), the critical isochore in (r, θ) space according to our model is given by

$$\theta \frac{\sum_{n=0}^2 P_{3n} \theta^{2n}}{\sum_{m=0}^2 P_{2m} \theta^{2m}} = C_2 r^{1+\beta} \frac{1 - b^2 \theta^2}{b^2 - 1} \quad (\text{B8})$$

For the special case $C_2 = 0$, i.e. an infinite slope for the rectilinear diameter, the critical isochore is simply the locus $\theta = 0$ (for $\zeta = 0$). With a nonzero C_2 , the critical isochore is a more complicated function of r and θ .

However, our objective is to determine the leading singularity in C_v^{sing} as a function of t as the critical point is approached, i.e. as $r \rightarrow 0$, along the critical isochore. From Eqs. (45) and (B8), asymptotically

$$t \sim \frac{r}{b^2 - 1} \left[1 - \frac{C_2 b^2}{(b^2 - 1)^2} r^{1-\beta} + \dots \right] \quad (\text{B9})$$

and, since $\beta < 1$, the leading-order singularity along the critical isochore is equivalent to that along the locus $\theta = 0$.

Upon evaluating the Jacobians of Eq. (B6), setting $\theta = 0$, and identifying the leading singularity, we find that

$$\begin{aligned} C_v^{\text{sing}} &= \frac{P_c C_3}{a_T T_c} r^{-\alpha} (1 - \alpha)(b^2 - 1) \frac{P_{10}}{P_{20}} \\ &= \frac{P_c C_3}{T_c} \frac{a_0}{a_T} t^{-\alpha} (b^2 - 1)^{2-\alpha} (2 - \alpha)(1 - \alpha) \end{aligned} \quad (\text{B10})$$

which establishes the result that C_v diverges along the critical isochore according to Eq. (38) and provides the constant of proportionality between C_3 and the amplitude of the divergence.

The thermodynamic properties of a variety of fluids in the critical region have been correlated by Levelt Sengers, et al. [26] From their Eqs. (1.2), (1.3) and (2.4a) we may write

$$C_v^{\text{sing}} = \frac{P_c}{T_c} \frac{A^+}{\alpha} t^{-\alpha} \quad (\text{B11})$$

where A^+ is their reduced amplitude. Noting from their Eq. (3.14a) that $a_0 = -f_0/ak$ and using their Eqs. (3.8) and (3.13), we find that

$$C_v^{\text{sing}} = \frac{P_c}{T_c} t^{-\alpha} (2 - \alpha) (1 - \alpha) (b^2 - 1)^\beta a_0 (a x_0^{-\beta}) \quad (\text{B12})$$

where a and x_0 are critical region parameters tabulated for a variety of fluids in their Table 34. Comparison of Eqs. (A12) and (A14) yields

$$C_3 = (b^2 - 1)^{\beta + \alpha - 2} a_T [a x_0^{-\beta}] = 0.7222 [a x_0^{-\beta}] \quad (\text{B13})$$

As explained in the following report, C_3 must be assigned a value before a fit of the pure vapor pressure curve is undertaken. For the fluids listed in Ref. 26, Table 34, we determine C_3 from Eq. (B13). Since $C_3 \approx 30$ for all of these fluids (except the helium isotopes), when we require a fit to a pure fluid not correlated in Ref. 26 we simply set C_3 equal to 30.

VLE correlations are not particularly sensitive to the choice of C_3 , since, in Eqs. (37) and (61), the terms in $(-t)^{2-\alpha} = (-t)^{1.9}$ and t^2 are highly correlated, and changes in C_3 can be compensated by alterations in C_5 . However, C_3 is very important for analysis of interfacial tension (IFT), for which the amplitude varies as $C_3^{2/3}$. Moldover and Rainwater [29] have analyzed the carbon dioxide + n-butane IFT data of Hsu, Nagarajan and Robinson [56] by means of the present model and concepts from the two-scale-factor universality theory of Stauffer, et al. [65], as verified by Moldover [66] for IFT data from pure fluids and binary mixture LLE. Except for one isotherm very near critical, the Nagarajan-Robinson data are predicted to within ten percent, comparable to their scatter. One could also invert the procedure and determine C_3 from IFT data.

Appendix C

Comparison of the Original and "Modified" Leung-Griffiths Models

Since the publication of the original Leung-Griffiths paper in 1973, there have been two rather distinct approaches to its use for VLE calculations. First, some researchers, in particular D'Arrigo et al. [27] and Chang and Doiron [28], have adhered very closely to the original Leung-Griffiths nomenclature and methodology, and have made changes only in the truncation points of certain polynomial fitting functions. We refer to this line of effort as the "original" Leung-Griffiths model. Second, Moldover and Gallagher [3,4] introduced rather substantial changes into the structure and philosophy of the model, including the introduction of the variable t , the use of corresponding states ideas, the possibility of a sloping rectilinear diameter, and the hypothesis, given further justification in this work, that $x = 1 - \zeta$ on critical. The present work has built onto this "modified" Leung-Griffiths model by adding features as necessary to accommodate mixtures farther from azeotropy.

The various modifications introduced by Moldover and Gallagher are largely independent of each other. Therefore, one could construct various hybrid models that include some, but not all, of their modifications. Nevertheless, it is our view that all of their modifications help to make the Leung-Griffiths model a more efficient and useful technique for VLE (and perhaps for one-phase thermodynamic) correlations.

The original Leung-Griffiths formalism follows the development of Sec. 2, except for the temperature-dependent K , up to Eq. (29). The variable t is not introduced in the original model; in contrast, τ is retained and largely plays the subsequent roles of t . For example in the construction of ω_{sing} by means of the Schofield linear model, our Eqs. (45)–(47), the original model uses in place of Eq. (45) the relations

$$\bar{\tau} = \ell(\zeta) \tau \quad (\text{C1})$$

$$\bar{\tau} = r(1 - b^2 \theta^2)/RT_{c1} \quad (\text{C2})$$

where $\ell(\zeta)$ is a linear function, but Eqs. (46) and (47) are retained apart from some notational difference.

For the initial theoretical development, i.e. Eqs. (11)–(28), τ is useful in that the necessary partial derivatives are kept relatively simple. But for purposes of correlation, t is clearly preferred as it is dimensionless whereas τ has dimension. Furthermore, by

corresponding states Eqs. (37) and (39) will have nearly the same coefficients for the pure fluids in terms of t , but not in terms of τ , particularly if the critical temperature ratio is large.

The presence of $\ell(\zeta)$ in Eq. (C1), therefore, may be viewed as a compensation factor for an artificial distortion of the model by use of τ instead of t . Such a distortion also adversely affects correlation of the regular part of ω . We see utterly no advantage in the use of τ in place of t , and strongly advocate that t be employed in future calculations.

The original formalism then expands $B_c(\zeta)$, Eq. (11), $H(\zeta, t)$, Eq. (12), and $\omega_{an}(\zeta, \tau, h)$ Eq. (41), in straightforward polyomial series in the respective independent field variables. The coefficients of these polynomials constitute the parameters of the model, and such polynomial fits are, respectively, analogous to our Eq. (96) for $B_c(x)$ and Eq. (86) for $x_c(\zeta)$, Eq. (95) for $\bar{H}(\zeta, t)$, and Eq. (42) for $\omega_{an}(\zeta, t, h)$, with $C_2(\zeta)$ given by Eq. (80) and $C_i(\zeta)$, $i > 2$, by Eq. (62). The original model does not introduce the functions \bar{Q} of Eq. (32) or \bar{H} of Eq. (34), and models $H(\zeta, \tau)$ rather than $\bar{H}(\zeta, t)$. From Eq. (34), a truncation of \bar{H} linear in t is equivalent to a truncation of H quadratic in τ .

Different truncation points of these polynomials are utilized in the fits by Leung and Griffiths to the helium 3 + helium 4 data of Wallace and Meyer [67,68], by D'Arrigo et al. to the carbon dioxide + ethylene data of Haselden et al., [69,70] and by Chang and Doiron to the carbon dioxide + ethane data of Khazanova et al. [71]. No specific guidelines have ever been given for these truncation points, and it is implied that they must be determined on a purely *ad hoc* basis for each separate mixture.

Leung and Griffiths [2] recognize the redundancy of the model due to the choice of K and zeroes of chemical potential, whereas the other groups evidently do not. Thus Leung and Griffiths specifically restrict $B_c(\zeta)$, and the inverse critical temperature, in their Eq. (3.6) to be linear in ζ . In their Appendix B, they point out that, with the above degrees of freedom and a constant K , such a linear relation can be satisfied approximately. The argument is similar to ours in Eqs. (35)–(36) and, in fact, for monotonic $T_c(x)$ a temperature dependent K may similarly be shown to exist such that inverse critical temperature is strictly linear in ζ .

However, the other two cited mixtures do not exhibit a monotonic $T_c(x)$. The evidence for a minimum in T_c of carbon dioxide + ethylene was inconclusive from the data of Haselden et al. [69,70], and D'Arrigo et al. [27] fit $B_c(\zeta)$ to a quadratic form so that a minimum occurs at pure ethylene. A subsequent experiment by Khazanova, et al. [72], clearly showed a minimum in T_c at ten percent carbon dioxide. While it was a significant accomplishment to show that the Leung–Griffiths model can describe azeotropy,

D'Arrigo et al., by removing any restriction associated with the degrees of freedom in K , made the formalism in principle highly redundant. Chang and Doiron went further in using a cubic form for carbon dioxide + ethane, which has a crescent-shaped P - T critical locus with a pronounced temperature minimum [71].

These three mixtures all have a relatively small α_{2m} and thus, according to this report and the following one, are relatively easy to fit. For helium 3 + helium 4, $\alpha_{2m} = 0.074$; for carbon dioxide + ethylene, $\alpha_{2m} = 0.07$; for carbon dioxide + ethane, $\alpha_{2m} = 0.053$. It would be expected that mixtures far from azeotropy, e.g. propane + n -octane, would require many additional terms in the polynomial series, and in the absence of guidelines quality fits would be quite difficult to achieve and a clear danger of overfitting would be present.

For the boundary conditions that yield pure-fluid critical and coexistence properties, the original model yields a cumbersome set of coupled equations, e.g. Eqs. (29)–(34) of Chang and Doiron [28], in place of our more direct representations of Eqs. (61)–(63), (76) and (80). While perhaps a minor point, this does further demonstrate the efficiency of the modified model over the original one.

In the discussions of relative merits, key issues have been the slope of the rectilinear diameter and the potential applicability of the model to the one-phase region. The sloping diameter is described by the term proportional to C_2 in Eq. (39) or (60), and originates from the term (th) in Eq. (42). The original model could include such a sloping diameter with a (τh) term in ω_{an} (or ω_r in the alternate notation). However, neither Leung and Griffiths (their Eq. (3.2)), nor D'Arrigo et al. (their Eq. (5)), nor Chang and Doiron (their Eq. (9)), choose to include such a term.

Again, for helium 3 + helium 4 this omission is justified, because C_2 for these pure fluids is exceptionally small [4]. For most ordinary fluids, $C_2 \approx -1$ and its omission leads to deviations from experiment, as was recognized by Chang and Doiron [28]. From visual inspection the ρ - x plot of their Fig. 8 presents a fit clearly inferior to the earlier fit of Moldover and Gallagher [4] (their Fig. 4) of the same mixture and data.

The three correlations with the original Leung–Griffiths model cited above consider the supercritical one-phase region as well as VLE. The research to date with the modified Leung–Griffiths model has not, although this has been largely at our election. As described in Part II of this series, while many VLE surfaces have been correlated, many more have not, and problems remain for correlating azeotropic mixtures, normal mixtures very near or very far from azeotropy, mixtures without coexisting density data, and VLE in the presence of LLE. Related problems include the correlation of multicomponent mixture VLE, interfacial tension, and coexisting enthalpy data, the investigation of formal

nonlinear least-squares fitting, and the merging of our model near critical with a classical equation of state away from critical. While correlation of the one-phase region is certainly an important problem, we have seen no cause for assigning it priority over these other important and interesting problems at present. In any case, it is quite premature to conclude that the modified Leung-Griffiths theory will not work in the one-phase region.

Throughout this project, it has been recognized that a sloping rectilinear diameter, or nonzero C_2 , in principle leads to problems in the one-phase region. For pure fluids, the $h = 0$ locus in the supercritical region represents a symmetry locus, that of inflection points of isotherms on a P - ρ diagram, that empirically is close to the critical isochore, whereas the present model in the supercritical region would incorrectly give a sloping line on such a diagram for that symmetry locus.

The generalization of revised scaling to mixtures, as discussed below Eq. (61), offers the most promising hope of escaping this dilemma. In unpublished work, Chang [73] has incorporated revised scaling, as well as a (τh) term, into the original Leung-Griffiths formalism. For carbon dioxide + ethane, an improved VLE fit is obtained comparable in quality to that of Moldover and Gallagher, as well as an improved fit of the mixture specific heat. Also in unpublished work, Moldover [74] has included revised scaling into the pure-fluid limit of the modified Leung-Griffiths model and has found good agreement with carbon-dioxide data and correlations in the supercritical region.

We recommend that a study of the one-phase region by means of the Leung-Griffiths model, if undertaken, be conducted along the lines of the present project. First, an appropriate extended critical region should be defined, e.g. $r < 0.1$ where r is the Schofield parameter of Eqs. (45)–(47). Second, an appropriate criterion for thoroughness of measurement over this region should be established. Third, P - T - ρ - x data from all sources should be collected, and, fourth, priorities should be assigned to the mixtures according to the proximity to azeotropy (smallness of α_{2m}) and thoroughness and reliability of the data. Pressures from programmatic considerations to focus on a particular mixture or narrow set of mixtures should initially be resisted.

The absence of a sloping rectilinear diameter in the original method may have given it some initial advantage in the one-phase region. However, within either method, the ultimate requirements will probably be both revised scaling and a (th) or (τh) term in ω_{an} . The more important modifications of the model, the use of t instead of τ and the incorporation of corresponding states, may well yield advantages for the one-phase region as well as for VLE. Just as it is a useful first approximation to assume that a *curve* of

constant ζ on the coexistence surface behaves as a pure fluid, it may be a similarly useful hypothesis that a *surface* of constant ζ behaves as a pure fluid in the near-critical one-phase region.

None of the statements in this appendix should be construed as criticism of the research efforts of Leung and Griffiths [2]. Clearly, the success of our project has depended on their understanding of field and density variables, their clever construction of ζ with its many useful properties, and numerous other relationships and insights. The primary motivation of the Leung-Griffiths paper was not to develop a general formalism for correlation of all binary mixtures. Rather, it was to reassert the predictions by Griffiths and Wheeler [12] of the behavior of specific heats at constant composition in view of some apparently contradictory data on helium 3 + helium 4 due to Wallace and Meyer [65,66]. It is therefore not surprising, and no reflection on Leung and Griffiths, that subsequent researchers have established a more efficient revision of the model for non-cryogenic binary mixtures.

Nevertheless, except perhaps for the modeling of H instead of \bar{H} (as discussed at the conclusion of Sec. 5), we see no particular advantages in the original Leung-Griffiths model over the present version. We strongly recommend that future research in critical phenomena of binary mixtures be conducted starting from the present, modified formalism.



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